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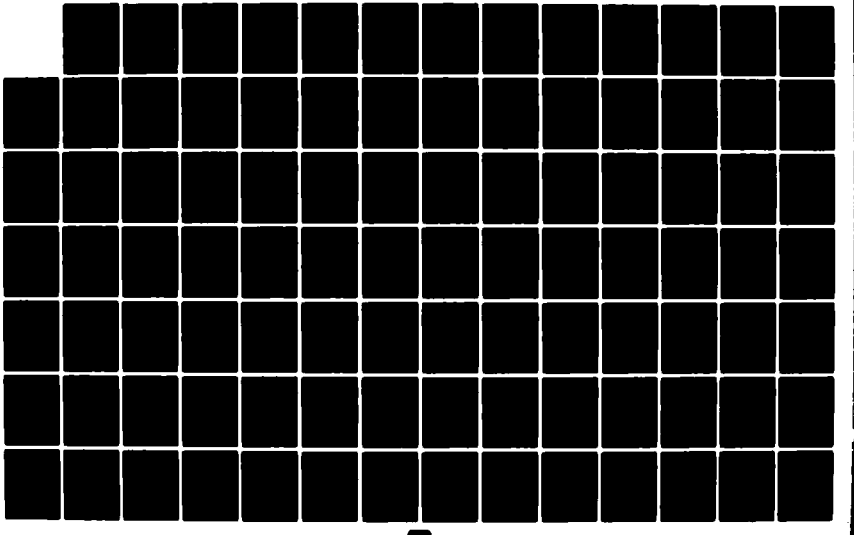

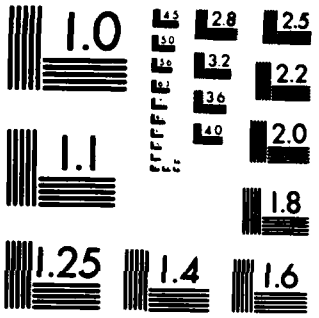

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RESEARCH AND DEVELOPMENT OF HAZARDOUS/TOXIC WASTE ANALYTICAL SCREENING PROCEDURES
Available Field Methods for Rapid Screening of Hazardous Waste Materials at Waste Sites (CLASS A POISONS)
INTERIM REPORT

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Bruce E. Schulte
Laura Mangoba
Edward T. McHale

January 1982

Supported by:

U.S. ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND
Fort Detrick, Frederick, Maryland 21701

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Contracting Officer's Technical Representative:
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ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
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ATLANTIC RESEARCH CORPORATION
Combustion and Physical Science Department
Alexandria, Virginia 22314

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A literature survey was undertaken to identify Class A poisons and to identify candidate field detection methods for each poison of interest to this study. The literature obtained on each candidate method was judged by the following criteria: method complexity, field adaptability, reagent shelf life, interference levels, detection sensitivity, reagent cost and reagent toxicity. Candidate procedures were found for arsine, bromoacetone, cyanogen chloride, ethyl and methyldichloroarsine, cyanogen, germane, hydrocyanic acid, nitric oxide, nitrogen dioxide,

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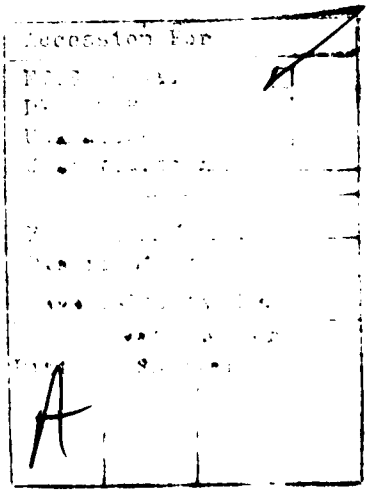
phosgene, diphosgene, phosphine, phenylcarbylamine chloride, dichloro (2-chloro-vinyl) arsine, dichlorodiethyl sulfide.



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EXECUTIVE SUMMARY

The objective of this ongoing program is to identify and evaluate various detection methods for the field screening of Class A poisons at uncontrolled hazardous waste disposal sites. For the purpose of the present study, the 16 Class A poisons defined by the Department of Transportation in Title 49 of the Federal Register were selected as the initial substances to be investigated. The Class A poisons are arsine, bromoacetone, cyanogen, cyanogen chloride, dichlorodiethyl sulfide (mustard gas), dichloro-(2-chlorovinyl) arsine (lewisite), diphosgene, ethyldichloroarsine, germane, hydrocyanic acid, methyldichloroarsine, nitric oxide, nitrogen dioxide, phenylcarbylamine chloride, phosgene and phosphine. The Department of Transportation defines Class A poisons as "poisonous gases or liquids of such nature that a very small amount of the gas, or vapor of the liquid, mixed with air is dangerous to life." Based on the above definition, the need for rapid field screening of Class A poisons is obvious when one considers the implication on both personal safety and transportation classification requirements.

A comprehensive literature survey was conducted on each of the poisons to identify candidate detection methods. The literature obtained on each poison was judged by the following criteria: method complexity, field adaptability, reagent shelf life, interference levels, detection sensitivity, reagent cost and reagent toxicity. Methodologies such as portable gas chromatography, organic vapor analyzers, infrared spectrophotometry and other sophisticated instrumental techniques were generally ruled out because of their inability to screen specifically for all Class A poisons at a given set of instrumental parameters. For example, it would be very difficult to have a one- or two-column portable gas chromatography system that would enable all 16 Class A poisons to be screened at one set of instrumental parameters. However, general detection methods such as infrared spectrophotometry could be used to determine the chemical functionality of the constituents within a complex sample. This information could be used to establish the need for additional more specific tests.

Animal testing was investigated as a means of screening for Class A poisons at hazardous waste sites. This approach would indicate the presence of potentially lethal wastes but would not be confined to the 16 Class A poisons of interest in this study. This approach would also not be acceptable as a general screening method for toxic substances since there would be no way to establish a physiological correlation between man and the test organism on the complex variety of unknown sample types anticipated at hazardous waste sites. Test organisms can be either more or less responsive to a specific substance than man. In addition, this approach is not conducive to a rapid field screening methodology.

The use of enzyme tests as an approach for screening for Class A poisons was considered during this program. The enzyme approach involves

selecting an enzyme that when introduced to a specific compound or class of compound becomes inhibited in its ability to produce a specific end product. Colorimetric reactions can then be used to detect the presence of this end product. Our literature survey of this approach did not indicate research that had been conducted testing Class A poisons. In addition, most of the work that has been conducted has been done using relatively clean aqueous matrices. It is unclear, at this point, what effect complex sample matrices may have on the inhibition of the enzymes activity. Therefore, the use of enzymes as a detection method for Class A poisons was not considered an imminent promising approach.

The Beckman Microtox™ Toxicity Monitor utilizes a specialized strain of luminescent bacteria as a bioassay organism. The total metabolic process of this bacteria is intrinsically tied to respiration but, unlike most other life forms, end products of metabolism include an appreciable quantity of light. The metabolism of the luminescent bacteria is influenced by low levels of toxicants which causes a corresponding change in the intensity of the organisms light output. The change of light output can be measured and used to determine the toxicological nature of the unknown sample. Obviously, the response mechanism of this method would not be tied to just Class A poisons but to all compounds which stressed the bacteria. Therefore, this approach could not be used to screen specifically for Class A poisons. The technique, however, might be useful as a means of general toxicity screening if the response factor between very toxic and slightly toxic substances could be sufficiently attenuated to reflect the differences.

The current state of the art for existing general detecting methods is not suitable for the specific field screening of Class A poisons. It appears that a specific detection method for each of the Class A poisons of interest to this study is the more promising approach. A convenient method for the field screening of specific volatile substances is the use of gas detection tubes. These tubes contain a granulated solid support such as silica gel coated with a reagent that changes color in the presence of the species the reagent is designed to detect. A known quantity of sample gas is drawn through the detection tube and the length of the resulting discoloration is read against a pre-calibrated scale to give the concentration of the species of interest. Following is a summary of the literature survey of the more promising detection reagent systems that might be utilized with the gas detection tube concept. Several of the Class A poisons have gas detection tubes which are already commercially available.

The survey showed that for hydrocyanic acid, 16 reagent detection systems lend themselves to field screening of this substance. Four of the methods considered dealt with photometric analysis, while the other procedures dealt with absorption of hydrocyanic acid and/or the detector reagent on some type of solid support such as silica gel, filter paper, or activated charcoal. All factors considered, the commercially available Draeger detector tube for hydrocyanic acid appeared to offer the greatest potential for incorporation into field methodology. This tube has a detection range of 2.3 to 34 mg/m^3 with acidic or basic potentially interfering gases, such as hydrogen sulfide, hydrogen chloride, sulfur dioxide and ammonia, being retained in the precleanse layer.

Ten reagent systems were reported for the detection of arsine. Three of these methods involve photometric analysis, one is a titration procedure, while the other six utilize absorption on a solid support as described above. The most promising of these methods for field screening use appears to be the Draeger arsine detector tube. This tube has a detection range of 0.16 to 195 mg/m^3. Phosphine and antimony hydride are listed as positive interferences. It should be noted that phosphine is also classified as a Class A poison.

A total of 16 detector reagent systems were located for the screening of ethyl and/or methyldichloroarsine. Two of these methods used a precipitate in the reagent solution as a positive result. Twelve of the methods utilized reagent-treated filter paper, while one used a coloration change made by marks of a treated crayon. The method which appears to be the most suitable for incorporation into a field test kit uses a detector tube containing silica gel which has been impregnated with a mixture of zinc sulfate and molybdic acid. This tube offers direct and sensitive detection for alkyldichloroarsines. The detection limit of the reagent is given as 2.5 µg; other closely related organo-arsenic halides and hydrogen sulfide are given as positive interferences.

For lewisite, 11 potential field screening methods were found for its detection. The most promising of these methods appears to be that which uses Michler's thioketone (4,4'-bis (dimethylamino) thiobenzophenone) as the reagent absorbed on silica gel. This reagent system is one that is currently used by the Army in its M256 gas detector kit for the detection of lewisite.

Seven methods were identified that could be used for the field detection of cyanogen chloride. Two of these methods required photometric analysis while one involved titration. The other four approaches used reagents absorbed on some type of solid support. The most promising approach appears to be the use of the cyanogen chloride detector tube made by Draeger. This tube has a detection range of 0.64 to 12.8 mg/m^3. Cyanogen bromide is listed as a positive interference.

Nitric oxide and nitrogen dioxide can be detected by using the Draeger nitrous fumes detector tube. A total of 15 reagent systems was examined for the detection of nitric oxide and/or nitrogen dioxide. The Draeger tube method appears to be the most advantageous approach since both gases can be detected simultaneously and the method is commercially available.

Eleven methods appeared suitable for adaption to field screening of phosphine. One of these methods involved titration, while two utilized photometric analysis. The remaining eight methods used liquid reagents absorbed on solid supports. The most promising method appears to be the use of the Draeger phosphine detector tube. This tube has a detection range of 0.14 to 5.68 mg/m^3. Antimony hydride and arsine, a Class A poison, are given as positive interferences.

Mustard gas was found to have 11 reagent detector systems that could be used for field screening of this compound. The most attractive of these methods appears to be silica gel impregnated with auric chloride. According

to the literature, a characteristic reddish-brown coloration is obtained in the presence of mustard gas.

Only four reagent detection methods were found for the field screening of bromoacetone. The best approach for the detection of this compound appears to be a two-step method. Sodium nitroprusside is used as a detecting reagent for methyl ketones in the first step. An orange coloration of the sodium nitroprusside indicates the presence of this class of compounds. The second step is the detection of bromine using fuchsin-sulfurous acid test paper. A positive response is indicated by formation of a violet color. When both of these tests are positive, bromoacetone is assumed to be present.

Sixteen reagent systems were examined for the detection of phosgene. Three of these methods require photometric analysis while one involves titration. The remaining approaches use a reagent on solid support. The best method appears to be the use of the Draeger phosgene detector tube. This tube has a detection range of 0.17 to 6.2 mg/m^3, with interferences listed as carbonyl bromide and acetyl chloride. Literature dealing with the detection of diphosgene stated the gas is heated 300 to 350°C in order to decompose it to phosgene, which is then detected by the above methods. The necessity of this heat treatment will have to be determined in the laboratory.

One method was located for the specific detection of cyanogen. The reagents used for this test are 8-quinolinol and potassium cyanide, which turns red in the presence of this species. In addition, cyanogen may be converted to hydrogen cyanide or cyanogen chloride and detected as these substances.

Five detection means were reported for germane. Two of these methods involved titrimetric analysis. At present, the most promising approach, for field detection, appears to be the use of the reagent, hydroxyphenyl fluorone, which turns an orange color in the presence of germanium.

Only one method was reported for the detection of phenylcarbylamine chloride. This method uses sudan red, ground chalk and $FeCl_3$ which turns from red to green in the presence of phenylcarbylamine chloride. Sudan red is listed as a carcinogen but utilization of the reagent in a gas detection tube would lessen the possibility of exposure during use.

It is recommended that the above methods be evaluated in the laboratory as a means of screening for the Class A poison for which each system is designed. This approach should be coupled with a vapor phase or gas stripping sampling technique to determine the effect that various solvent matrices may have on each of the detection methods. General screening protocol, such as infrared spectrophotometry, should be investigated to determine if this approach is useful as means of determining when it is necessary to perform a specific test for a Class A poison.

FOREWORD

This program was undertaken in order to evaluate methods suitable for the field analysis of Class A poisons at hazardous waste sites. The study was performed in fulfillment of Contract No. DAMD17-78-C-8075 and was conducted from January 1981 through January 1982, with Mr. Danny L. Laspe, U.S. Army Medical Research and Development Command, as the Contracting Officer. Dr. Katheryn Kenyon, U.S. Army Medical Engineering Research and Development Laboratory, served as the Contracting Officer Technical Representative. Citations of commercial organizations and trade names in this report do not constitute an official Department of the Army endorsement or approval of the products or services of the organizations.

The information in this document has been funded wholly or in part by the United States Environmental Protection Agency under assistance Agreement number AD-21-F-1-304-0 to the U.S. Army, it has been subject to the Agency's peer and administrative review, and it has been approved for publication. The contents reflect the views and policies of the Agency.

PREFACE

Much attention has been focused on the hazards of chemical waste disposal. Many of the disposal practices that were acceptable twenty years ago are now subject to much criticism. This is primarily due to technology being better able to define the environmental impact of past disposal processes. The main concern today is the protection of the health of the people and the environment around these chemical dumping sites. In many cases, urban development has precipitated the current problem by expanding into regions too close to these disposal sites. Resolution of suspect chemical storage sites generally requires that such sites be cleaned up or recontainerized so that the chemicals do not pose a threat.

Class A poisons at waste sites create an additional problem because of the toxicological inhalation hazard they present to waste handlers and because of the packaging requirements associated with their transport. One breath of the concentrated vapors of a Class A poison could be instantaneously lethal to a waste handler. The opening of sealed containers at waste sites, containing unknown substances, presents a situation where exposure to high concentrations of these materials could occur. It is desirable, therefore, to have methods for the in situ screening of Class A poisons at waste sites prior to handling or packaging operations.

The presence of Class A poisons at waste sites is no longer a question to be debated since confirmed occurrences have been documented. The purpose of this report is to define the Class A poisons and to select candidate field screening methods that might be used at waste sites to detect these highly toxic substances.

CONTENTS

FIGURES

TABLES

(continued)

FIGURES

TABLES

(continued)

TABLES (continued)

LIST OF ABBREVIATIONS[4]

atm = atmospheres (pressure)
cns = central nervous system effects
°C = degrees centigrade
D = λ 589.3 mμ
decomp. = decomposes
eye = eye effects
g = gram
g/l = grams/liter
h = hour
hmn = human
i = intermittent
ihl = inhalation
ims = intramuscular
indust. = industrial
int = intermediate
ipr = intraperitoneal
irr = irritant effects
ivn = intravenous
kcal/mol = kilocalories per mole
kg = kilogram (one thousand grams)
l = liter
LC_{50} = lethal concentraton 50 percent kill
LC_{Lo} = lowest published lethal concentration
LD_{50} = lethal dose 50 percent kill
LD_{Lo} = lowest published lethal dose
M = Molar
min = minute
m^3 = cubic meter
MAC = maximum allowable concentration
mfr. = manufacture
mg = milligram (one thousandth of a gram: 10^3 gm)
misc. = miscellaneous
mixt. = mixture
ml = milliliters
mm Hg = millimeters of Mercury
mus = mouse
neo = neoplastic effects
orl = oral
ppm = parts per million (v/v)
rat = rat
rcb = red blood cell effects
rbt = rabbit
scu = subcutaneous
skn = skin effects
std-air = standard air in TLV measurements
TC_{Lo} = lowest published toxic concentration
TD_{Lo} = lowest published toxic dose
tfx = toxic effects
TLm = Tolerance limit median for a 96 hr. exposure period
TLV = threshold limit value (maximum 8 hour human exposure level)
wk = week
μg = microgram

SECTION 1

INTRODUCTION

A necessary first step in the investigation of hazardous waste disposal sites requires that the contents of such sites be characterized. The unlabeled hazardous wastes in closed containers at various sites throughout the country requiring laboratory analysis present a formidable challenge in both time and expense. The testing of each unlabeled hazardous waste would require the removal of a sample from the container for analysis in the field or for return to a central laboratory for in-depth characterization.

A significant problem associated with the removal of unknown substances from these waste sites is personal safety. This is because, at the time of sampling, the relative toxicity at the site is unknown and, therefore, could present a significant health hazard. For example, if a site contained a Class A poison of which a very small amount of gas or vapor of the liquid mixed with air is dangerous to life, then it would have to be handled differently than Class B poisons. For safety considerations, the presence or absence of Class A poisons at these sites should be established immediately upon sampling. In addition, special packaging requirements must be met before Class A poisons may be legally transported. Therefore, before a waste can be shipped to a central laboratory for analysis, the shipper must know what hazard category in which to place the waste to insure shipping safety.

It would, therefore, be beneficial to have simple rapid analytical methodologies available for the screening for Class A poisons prior to return of the sample to a central laboratory facility for more thorough characterization.

In order to fulfill this purpose, a study was performed by Atlantic Research Corporation from January 1981 to January 1982 under USAMRDC Contract No. DAMD17-78-C-8075. The objectives of this program were to:

- Define all Class A poisons
- Survey the literature for candidate detection methods that might be used in the field to screen for specific Class A poisons
- Make recommendations, based on the literature reviewed, for a practical approach to screening for specific Class A poisons in unknown hazardous wastes.

SECTION 2

CONCLUSIONS

The following general conclusions can be formed from the results of this study.

(1) General screening procedures for Class A poisons, while highly desirable, do not exist. However, the Microtox™ toxicity monitor does show some promise for screening unknown wastes for highly toxic substances but not specifically for Class A poisons. This method would appear to be the most advantageous for utilization as a general screening method for highly toxic substances. Determining the feasibility of the Microtox™ for this purpose would require an in-depth laboratory development and evaluation program.

(2) The enzyme ticket approach may also prove to be a favorable screening technique. Unfortunately to date, only a few enzymes have been investigated for their detection capabilities. A full scale development and evaluation program would have to be conducted to determine what enzymes to use and under what type of test conditions. This approach currently has too many unresearched variables to be considered for our purposes.

(3) It appears that the best state-of-the-art approach to screening for specific Class A poisons is to use a reagent detection system designed for each poison or similar group of poisons. This appears to be the best trade-off between detection sensitivity, specifity and method simplicity currently available. The ideal reagent detection system would be utilized in the form of gas-detector tubes, which would permit pre-packaging of test methods and minimal effort at the sampling site.

SECTION 3

RECOMMENDATIONS

A systematic test approach is necessary for testing of unknowns for Class A poisons. This approach can be divided into the following general areas for which specific recommendations are made:

(1) Sampling - The sampling of headspace gases is the recommended approach for determining the presence of Class A poisons in containers at waste sites.

(2) General Screening Procedures - It is recommended that enzyme tests and the Microtox™ monitor be investigated as general screening approaches for establishing the presence of very toxic substances. It is also recommended that infrared spectroscopy be investigated as a general technique for establishing the absence of specific Class A poisons in an unknown.

(3) Specific Screening Tests - It is recommended that the analytical tests outlined in this report be evaluated, modified where necessary, and qualified as field test methods for specific Class A poisons.

SECTION 4

CLASS A POISONS

The initial task of this study was to identify those compounds that have been categorized by various authorities as Class A poisons. To accomplish this, a manual and computerized literature search was conducted. The Manufacturing Chemists Association and various officials responsible for shipment of chemicals from private chemical firms were also contacted to determine what guidelines are used in classifying substances as Class A poisons. It was felt that people concerned with transport of chemicals would be especially cognizant of hazards concerning Class A poisons, as shipping regulations must be complied with before hazardous substances may be shipped.

It was found that two sources are used to classify the hazardous nature of substances to be shipped. These are the Department of Transportation (DOT), Title 49 of the Code of Federal Regulations[1], and the International Air Transport Association (IATA)[2]. The DOT regulates shipment by common carriers in rail, truck, barge, and air while IATA regulates the international air shipment of hazardous materials. In addition to a general definition to be used for categorizing compounds that are not listed, each of these sources lists specific compounds which are referred to as Class A poisons. Both of these organizations use the same general definition for Class A poisons. These poisons are defined as being "extremely dangerous poisonous gases or liquids of such nature that a very small amount of gas or vapor of the liquid mixed with air is dangerous to life." In the event that a substance to be shipped is not specifically listed at a certain hazard level, it is the responsibility of the shipper to determine the substance category. Although DOT and IATA use the same definition for Class A poisons, their listings of these substances vary. For instance, Chloropicrin is categorized as a Class A poison by IATA, but is a Class B poison according to DOT. Table 1 lists those compounds which DOT classifies as Class A while Table 2 lists IATA's Class A poisons.

Another source consulted for specific compounds classified as Class A poisons was Dangerous Properties of Industrial Materials by N. Irving Sax[3]. The third edition of this book lists 23 compounds as Class A poisons which are given in Table 3. These compounds were classified as Class A poisons in a subsection of the book dealing with shipping regulations. It should be noted that some of these compounds were not listed as Class A poisons by either of the other sources. The fifth edition of this book lists no compounds as Class A poisons, but then neither does it have the subsection describing the shipping regulations of each compound in the book. Ultimately, it would appear that this book has been rewritten so that the user must determine his own hazard classification for the compound being considered.

TABLE 1. TITLE 49 CLASS A POISONS[1]

Arsine

Bromoacetone

Cyanogen

Cyanogen chloride

Dichlorodiethyl sulfide (Mustard gas)

Dichloro(2-chlorovinyl)arsine (Lewisite)

Diphosgene

Ethyldichloroarsine

Germane

Hydrocyanic acid

Methyldichloroarsine

Nitric oxide

Nitrogen dioxide

Phenylcarbylamine chloride

Phosgene

Phosphine

TABLE 2. IATA CLASS A POISONS[2]

Arsine

Bromoacetone

Carbonyl fluoride

Chloropicrin

Cyanogen

Cyanogen chloride

Dichlorodiethyl sulfide (Mustard gas)

Diphosgene

Ethylbromoacetate

Ethyldichloroarsine

Germane

Hydrocyanic acid

Methyldichloroarsine

Nitric oxide

Nitrogen dioxide

Nitrogen trioxide

Nitrogen tetroxide

Phosgene

Phosphine

Phenylcarbylamine chloride

Tetrachlorodinitroethane

Trichloroacetyl chloride

TABLE 3. SAX CLASS A POISONS[3]

Allyl isothiocyanate

Arsine

Bromoacetone

Chloropicrin

Cyanogen

Cyanogen chloride

Dichlorodiethyl sulfide (Mustard gas)

Dichloro(2-chlorovinyl)arsine (Lewisite)

Diphosgene

Ethyl bromoacetate

Ethyldichloroarsine

Hydrocyanic acid

Hydrogen selenide

Methyldichloroarsine

Nitric oxide

Nitrogen dioxide

Nitrogen tetroxide

Phenylcarbylamine chloride

Phosgene

Phosphine

Tetrachlorodinitroethane

Trichloroacetyl chloride

It becomes evident by examining the Class A poisons from each source that some Class A poisons appear in all three listings while others are only classified by one source. For example carbonyl fluoride, is listed as Class A poisons in IATA, but no mention is found of it in DOT Title 49. Numerous compounds listed as Class B poisons are considered Class A poisons if they are found incorporated into a compressed gas. Hexaethyl tetraphosphate is such an example.

Due to the general nature of the definition of Class A poisons and the lack of coordination between DOT's, IATA's, and Sax's lists of these compounds, a decision was made to select the compounds that would be considered for the purpose of developing field screening methods. Personnel from EPA, the U.S. Army, and Atlantic Research Corporation mutually agreed upon selecting those compounds which are presently or have in the past been classified as Class A poisons by DOT. Substances which had to be mixed with a compressed gas to be considered Class A poisons were excluded, due to the unliklihood of finding these mixtures at waste sites. Table 1 lists those compounds which were mutually agreed upon as being the Class A poisons of interest during this study. Table 4 describes each of the Class A poisons identified during this survey and their general properties. Page ix describes the abbreviations used in Table 4. Table 5 lists Class A poisons identified at waste sites by the Environmental Protection Agency's Field Investigation Teams (the information given in Table 5 was compiled from data supplied by Dr. Barbara Elkus, Office of Waste Programs Enforcement Support Branch, Environmental Protection Agency, Washington, D.C.) The data in Table 5 does not imply that these are the only occurrences of Class A poisons at all waste sites being studied. It cannot be confirmed that all samples from all waste sites were screened for these specific substances. The data in Table 5 serves only to indicate that Class A poisons do exist at uncontrolled waste sites.

Appendix A of this report gives excerpts from DOT Title 49 for packaging and shipping requirements of hazardous substances. Appendix B presents a synopsis of DOT Title 49 Regulations as related to the transport of unknown substances by hazard category.

Table 4. Class A Poisons

Class A Poison	Formula	M.P. °C	B.P. °C	V.P mm	Toxcity [4]	Synonym
1. Arsine	AsH_3	-116.3	- 55.0	760 at-62.1°C	ihl-mus LD_{Lo} 70mg/m^3/3H ihl-hmn TC_{Lo}230,000mg/m^3 TFX-Sys	Arsenic hydride
2. Bromoacetone	$CH_2BrCOCH_3$	- 54.0	136.0	9 at 20°C	ihl-mus LC_{Lo}600mg/m^3	Bromo-2-propanone
3. Carbonyl fluoride	COF_2	-114.0	- 83.0	760 at 20°C	ihl-rat LC_{50} 972mg/m^3/1H	Fluoroformyl fluoride
4. Chloropicrin	CCl_2NO_2	- 64.0	112.0	40 at 33.8°C	ihl-mus LC_{50} 1600mg/m^3/10m ihl-hmn LC_{Lo}2400mg/m^3/m	Nitrochloromethane
5. Cyanogen	NCCN	- 34.4	- 21.0	760 at-21.0°C	ihl-hmn TC_{Lo}34mg/m^3 TFX:IRR	Ethane dinitrile
6. Cyanogen chloride	CNCl	- 6.5	13.1	1011 at 20°C	ihl-mus LC_{Lo}780mg/m^3/7.5M ihl-hmn TC_{Lo}10mg/m^3 TFX-Eye	Chlorine cyanide
7. Dichlorodiethyl sulfide	$S(CH_2CH_2Cl)_2$		228.0	~0.09 at 30°C	ihl-mus TC_{Lo} 189mg/m^3/10m ihl-hmn LC_{Lo}1500mg/m^3/m	Distilled mustard gas
8. Ethyl bromoacetate	$CH_2BrCOOC_2H_5$		158.8	Not Available	SCU-mus TD_{Lo} 332mg/kg/83WI TFX-NEO	Ethyl bromoethanoate
9. Ethyldichloroarsine	$C_2H_5AsCl_2$	- 65.0	156.0	2.29 at 21.5°C	ihl-hmn LC_{Lo} 100mg/m^3/30m ihl-mus LC_{Lo}160mg/m^3/10m	Dichloroethylarsine
10. Germane	GeH_4	-165.0	- 88.0	760 at-88.9°C		Germanium hydride
11. Hydrocyanic acid	HCN	- 13.2	25.7	400 at 10.2°C	ihl-hmn LC_{Lo}120mg/m^3/4 ihl-hmn LC_{Lo}200mg/m^3/10m ihl-mus LC_{Lo}150mg/m^3/10m	Hydrogen cyanide
12. Methyldichloroarsine	CH_3AsCl_2	- 59.0	136.0	10 at 24.3°C	ihl-mus LC_{Lo}270mg/m^3/10m	Methylarsenic dichloride
13. Nitric oxide	NO	-161.0	-151.8	760 at-151.7°C	ihl-mus LC_{Lo}393mg/m^3	
14. Nitrogen dioxide	NO_2	- 9.3	21.0	400 at 80.0°C	ihl-hmn LC_{Lo}376mg/m^3/m ihl-mus LC_{Lo}470mg/m^3/30m	
15. Nitrogen tetroxide	N_2O_4	- 11.2	21.15	760 at 21.0°C	ihl-rbt LC_{50} 1184mg/m^3/15m	
16. Nitrogen trioxide	NO_3			760 at 20°C	Not Available	
17. Phosgene	$COCl_2$	-104.0	8.3	1180 at 20°C	ihl-hmn LC_{50} 3200mg/m^3	Carbonyl chloride
18. Diphosgene	$ClCO_2CCl_3$		128.0	10.3 at 20°C	ihl-mus LD_{Lo}344mg/m^3	Trichloromethyl chloroformate
19. Phosphine	PH_3	-132.5	- 87.5	15,200 at-3°C	ihl-hmn LD_{Lo}1391mg/m^3	Hydrogen phosphide
20. Phenylcarbylamine chloride	$C_6H_5NCCl_2$		208.0-210.0	Not Available	ihl-hmn TC_{Lo}50mg/m^3/10m TFX-IRR	Phenylimino phosgene
21. Trichloroacetyl chloride	CCl_3COCl		118.0	Not Available	ihl-mus LC_{Lo} 498mg/m^3/30m	
22. Tetrachlorodinitroethane	$(CCl_2NO_2)_2$	130.0		Not Available		
23. Allyl isothiocyanate	CH_2CH_2NCS	- 80.0	150.0	10 at 20°C	ipr-mus LD_{Lo}4mg/kg	Allyl mustard oil
24. Dichloro(2-chlorovinyl)arsine	$C_2H_2ASCl_3$		190.0	0.4 at 20°C	ihl-mus LC_{Lo}150mg/m^3/10m ihl-hmn LC_{50} 508mg/m^3/30m	Lewisite
25. Hydrogen selenide	H_2Se	- 64.0	-41.4	7600 at 23.4°C	ihl-hmn TD_{Lo}1mg/m^3 TFX-CNS	

TABLE 5. CLASS A POISONS IDENTIFIED AT WASTE SITES

CLASS A POISON	NUMBER OF KNOWN OCCURRANCES
Cyanogen	1
Cyanogen chloride	1
Hydrogen cyanide gas	1
General cyanide wastes	280
Nitric oxide	1
Nitrogen dioxide	1
Phosgene	5
Mustard gas	1

SECTION 5

GENERAL SCREENING METHODS

There are sixteen Class A poisons of current interest to this study. The ultimate objective of this program is to develop and evaluate analytical methods that can be easily utilized in the field to screen for these substances. Obviously, it would be advantageous to have a single general screening strategy which could be used to determine the presence of many of the Class A poisons concurrently. The ability to run one test or even use a single piece of instrumentation in the field would provide the personnel conducting field analyses a time efficient and simple means of screening for Class A poisons. The merits and disadvantages of current methodologies which appear useful for the general screening of unknown wastes to detect specific Class A poisons are discussed in the following sections.

TOXICITY MONITOR

The Beckman Microtox™ Toxicity Monitor is a device that can screen unknowns for their toxicological properties. This unit contains a set of interdependent enzyme systems controlling measurable physiological parameters, along with an appropriate measurement system. This monitor utilizes a specialized strain of luminescent bacteria as the bioassay organism. The total metabolic process of these bacteria are intrinsically tied to respiration, but, unlike most other life forms, the end products of metabolism include an appreciable quantity of light. Light can be measured more sensitively with simple instruments than any other physiological parameter. The metabolism of the luminescent bacteria is influenced by low levels of toxicants. Any alteration of metabolism in turn affects the intensity of the organisms' light output. By measuring changes in light output, the presence and relative concentration of toxicants can be detected.

To conduct a test using this instrument, the Microtox™ reagent is prepared by reconstituting a vial of lyophilized luminescent bacteria with 2 ml of reconstitution solution. This solution contains buffers, stabilizers, and activators. The vial is allowed to stabilize for 2 to 3 minutes in a cooling block (several vials can be prepared at once). The vial is then placed into the sample carrousel of the monitor and the carrousel turned to expose the vial to the photomultiplier tube. Total light output is read from either a digital panel meter or an accessory chart recorder. The sample to be tested is then injected into the vial through a light-tight port. If the sample is sufficiently toxic, a new baseline light-output will be established. Toxicity is reported as a percent decrease in light-output.

The Beckman Microtox™ Monitor appears to offer many advantages for screening unknowns to determine their toxicological nature. However, the use of the instrument for screening wastes to determine the presence or absence of Class A poisons does not appear feasible. All Class A poisons would probably give positive results using this technique but many other toxic, non-Class A compounds would react similarly. The monitor does not appear capable of distinguishing a particular compound nor does it lend itself to modification for this capability.

VAPOR ANALYZER/CHROMATOGRAPHIC TECHNIQUES

Vapor analyzers are commercially available portable units that are currently being used by the Environmental Protection Agency's Field Investigation Teams (FIT) for investigating hazardous waste sites. These units are used primarily to detect the presence of air contamination at those sites which might be a potential health hazard. As a rule, they do not determine the exact nature of the contaminant and, therefore, offer little in the way of screening for specific compounds. The one exception to using the vapor analyzer in a general screening configuration is when the exact nature of the contamination at a site is known in advance. In this case, the vapor analyzer can be used to locate isolated areas of that substance at high concentration. However, even this approach is questionable as a means of screening for specific substances at a given hazardous waste site.

The two major detection methods used in commercially available vapor analyzers are the flame ionization detector and the ultraviolet photoionization detector. Flame ionization, which is sensitive to the presence of organic vapors, is probably the most widely used detector. This detector is made up of three major systems, the hydrogen delivery, sample delivery, and the electronic amplification and display systems. The hydrogen system provides hydrogen to be burned with air provided by the sample delivery system. This results in the ionization of organic molecules in the air sample; the ions are collected by an electrode in the detector. The current generated by the ions is proportional to the concentration of vapor in the air sample. The photoionization detector sometimes used in vapor analyzers is a non-electrode discharge tube excited by a highly stable, ultra high frequency oscillator to emit ultraviolet light. This source supplies sufficient energy to ionize a wide range of species (organic and inorganic), but is insufficient to ionize permanent gases.

Neither of the above detectors offers much in the way of specificity in screening for the presence of specific Class A poisons or toxic substances in general. The problem is that both detectors will register the presence of about any substance that is present. Most vapor analyzers, however, are equipped with a chromatographic column option which permits the analysis of individual compounds. Basically, as the sample moves through the column its constituents are separated based on their interaction with the column packing material. The constituents leave the column and are carried to the detector where they are registered and recorded. The retention time is the time between sample injection and data readout. This is used to identify the

compound. A recorder gives the chromatogram which is used to compute the retention time. Various types of columns are available so that a specific compound can usually be determined chromatographically if the sample matrix is consistent from sample to sample. There are two distinct disadvantages associated with the use of chromatographic techniques on samples from different origins. The first disadvantage is that in working with samples from different sources, such as those found at hazardous waste sites, one can never be sure that another compound is not present in the sample that has the identical chromatographic retention time of a Class A poison. Several chromatography columns with different packing materials are generally used to reinforce the presence of a constituent in samples of this nature. The second disadvantage is that a single chromatographic column is not available which separates each of the 16 Class A poisons in such a manner that they can be analyzed individually in one analysis. Thus, it appears that chromatographic separation techniques would probably require the use of many columns to determine the presence of each Class A poison in a single sample. The changing of chromatographic columns and their associated operating parameters in a field environment would not be conducive to a rapid screening methodology. Table 6 lists several of the Class A poisons and the parameters used for their chromatographic analysis. No chromatographic information was found on the other Class A poisons in the literature reviewed.

INFRARED ANALYZER

The Foxboro Miran-80™ computing gas analyzer appears to have several good qualifications as an instrument for measuring Class A poisons. First of all, it is capable of measuring a wide range of toxic vapors and gases, including several Class A poisons. It can also measure concentration with a sensitivity below one part of the measurable species in one million parts of air (ppm) and give this information in the form of a computer printout on the spot. Last of all, it is lightweight, durable and easy to use.

The Foxboro Miran-80™ computing gas analyzer works on the principle that specific compounds absorb light at particular wavelengths and this absorption is a characteristic of that compound. In this instrument, an air sample is brought into the gas sample cell where it is exposed to infrared radiation at various wavelengths. The radiation is then absorbed at the wavelength characteristic of the compound(s) being exposed. This absorption value is converted into concentration values of ppm or percent for direct meter readout by the computer. Concentration values are calculated based on previously recorded absorption spectra of the identical compound at a known concentration.

Although this instrument has several outstanding qualities, there is one major disadvantage. This is the possibility of interference caused by other materials with absorption bands overlapping the absorption bands of the compounds of interest. Since the Class A poisons are likely to be located in areas (drums, etc.) with other compounds of varying concentration, this could very easily happen.

For example, phosphine absorbs at 10.1 μm and sec-butyl alcohol also absorbs at 10.1 μm. This would cause interference with or masking of the spectrum of the phosphine, depending on the concentration of the sec-butyl alcohol. Therefore, the analysis for the phosphine would probably be in error. It would be impossible to predict or plan for unknown interfering species that might be present with Class A poisons located at every hazardous waste site throughout the country. Should this approach be followed, one could spend more time looking for interfering species to determine if a particular analysis was valid than one would spend analyzing for the Class A poisons. It therefore appears that this approach is not adaptable for the purpose of establishing the presence of Class A poisons in unknown samples with complex matrices. The technique, however, may be useful for establishing that a specific Class A poison is not present if a characteristic absorption band is absent in the infrared spectrum of the sample.

MASS SPECTROMETRY

Mass spectrometry probably provides more molecular structure information than any other analytical technique for the analysis of organic and inorganic species. The information generated from the mass spectrometer is usually sufficient to determine the structure of the species being examined empirically.

The mass spectrometer (electron impact ionization) fragments a molecule to produce charged ions, usually consisting of the ionic form of the parent species and various other ionic fragments. The ion fragments are then sorted according to the mass-charge ratio and recorded as a "mass spectrum". The mass spectrum is a measurement of all the different mass fragments and their relative intensities. No two species exhibit identical spectra and, thus, mass spectra are suitable for the positive identification of any species detected. Generally, the larger the molecules being fragmented, the more complex the resulting mass spectrum.

All of the Class A poisons of interest to this study would be detected and would exhibit characteristic spectra.

Unfortunately, the fragmentation process occurs on all species present in the ionization source of the mass spectrometer. In the case of complex samples, such as those anticipated at hazardous waste sites, this results in the simultaneous generation of mass fragments from many species which get recorded in a single mass spectrum. The qualitative unraveling of such a spectrum can be an arduous task for even the most experienced mass spectroscopist. This is especially true when one considers that the species of interest would possibly be present in minute amounts when compared to other constituents present in the sample. There is a significant chance that the minor constituents would be masked by those present in larger concentration. The problem becomes one of separating the contribution of a Class A poison to a specific molecular fragment from the contribution by other constituents in the sample to the same molecular fragment. Many computer programs have been written which supposedly accomplish this task on mixtures containing, for example, seven separate species. The degree of success, even with computer

TABLE 6. G.C. COMPARISON CHART OF CLASS A POISONS

CLASS A POISON(S)	DETECTOR	COLUMN	COLUMN CONDITIONS	REF. NO.
Arsine AsH_3 Phosphine PH_3	Photo Ionization	4.3 meters X 2.5 mm i.d. TFE Column packed with 5% SE-300N Chromosorb 6, AW, DMCS, 60/80 mesh	24°C	5
Cyanogen NCCN Hydrogen cyanide HCN	Stainless steel dual column detector block with two matched-pair tungsten filament elements	Two columns: 1. .64 meters X 5 mm copper tubing 2.4 meter long filled with 30-60 mesh Chromosorb P impregnated with 25% triacetin. 2. .64 meters X 5 mm copper tubing filled with a molecular sieve.	Temperature Column #1 - 75°C Column #2 - room temperature. Carrier gas - He Flow rate - 400 ml/min	6
Hydrogen cyanide HCN	Thermal cond. detector	Two columns: 1. 2 meters column of polyethylene glycol on diatomite. 2. 1.8 meters column of molecular sieve	Temperature Column #1 - 120°C Column #2 - room temperature Carrier gas - He Flow rate - 400 ml/min	7
Hydrogen cyanide HCN	Not available	Two columns: 1. 2.4 meters X 6.1 mm copper tube with 20% polyethylene glycol 1500 on 30-60 mesh celite. 2. Same as above except on Linde molecular sieve 5A.	Temperature - 100°C Carrier gas - He Flow rate - 160 ml/min	8

(continued)

TABLE 6 (continued)

CLASS A POISON(S)	DETECTOR	COLUMN	COLUMN CONDITIONS	REF. NO.
Phosgene $COCl_2$	Electron capture detector	Not available	Not available	9
Phosgene $COCl_2$	Not available	Two columns: 1. Brick with 20% dibutyl sebacate. 2. Molecular sieve 5A, particle size 0.25-0.5m.	Temperature - 25°C Carrier gas - H Flow rate - 70 ml/min.	10
Phosphine PH_3	Thermistor cell	Stainless steel 4.0 meters x 6.1mm filled with fire brick 40-60 mesh with Apiezon L 30% Apiezon L 30%	Temperature - 35°C Carrier gas - He Flow rate - 25 ml/min.	11
Phosphine PH_3	Aerograph P	1.5 meters x 4.3mm Pyrex glass filled with 5% Dow 200 on Acropak 70-80 mesh.	Temperature - 190-250°C Carrier gas - N_2& He Flow rate - 20 ml/min N_2, 170 ml/min He.	12

(continued)

TABLE 6 (continued)

CLASS A POISON(S)	DETECTOR	COLUMN	COLUMN CONDITIONS	REF. NO.
Nitrogen oxide NO	Ar ionization cell	1.5 meters long No. 5A molecular sieve column.	Temperature - 100°C	13
Nitrogen dioxide NO_2	Not available	3 meters column of molecular sieve 5A, 20-40 mesh with 2 ml of H_2) in the anterior end	Temperature - 23°C Carrier gas - He Flow rate - 60 ml/min	14
Nitrogen dioxide NO_2 Nitrogen oxide NO	Not available	Column with two layers of silica gel separated by I_2O_5	Not available	15
Phosgene $COCl_2$	Thermal-cond. detector	Three columns of (charcoal, SiO_2 gel) and (silicone oil M.S. 200, 3 and 30%)	Not available	16
Phosgene $COCl_2$	Not available	3 meters x 3.0 mm column packed with celite 545 with dinonyl phthalate.	Not available	17

assistance, is contingent upon how closely the molecular fragments of the compound of interest matches those of the other species present. In a best case situation, the other species would be few in number and be present at a concentration that would not totally mask all of the identical mass fragments of the Class A poison. It is easily seen, in working with unknown samples of the complex nature anticipated at hazardous waste sites, the best case situation is not likely to be the rule.

Alternate mass spectrometry ionization methods, such as chemical ionization, generally result in fewer mass fragments from a given molecular species. This would result in a less complicated mass spectrum with less tendency of one mass fragment to mask the presence of another mass fragment. Generally, in this case, the molecular ion fragment plus one mass unit is the mass fragment that would be used to indicate the presence or absence of a specific compound. However, less fragmentation of the molecule also means that less information will be available to determine if and when a species other than a Class A poison is present that gives a similar response at the identical place in the mass spectrum. It is felt that the complex nature of the samples being considered for this study would preclude the use of the mass spectrometer as a means for the rapid and direct detection of Class A poisons in the field.

Another point should be made about the inherent sophistication of mass spectrometers. Mass spectrometers are analytical instruments that function through precise electronic timing circuits coupled with sophisticated vacuum and sample inlet systems. They are generally problematic in nature and require the talents of a well trained technician to diagnose and correct difficulties when they occur. Mass spectrometers should not be considered as candidates for continued field use in the screening of Class A poisons due to the inherently fragile nature of the instrumentation required.

SCREENING FOR CLASS A POISONS USING ORGANISMS

The use of animal testing for screening of Class A poisons was investigated as a means of detecting dangerous concentrations of Class A poisons present at a hazardous waste site. This type of screening would involve exposing test organisms to a quantity of hazardous waste to determine the lethal effect on the organisms. Ideally, the test would consist simply of adding a known amount of an unknown sample to the atmosphere of the organisms and determining the lethal effect after a set period of time.

This method may appear superficially attractive, but it has numerous limitations. A general assumption would have to be made that humans and the test organism selected react similarly to all Class A poisons. Toxicity data for Class A poisons show a clear lack of correlation between the physiological reaction of man and other organisms. A lethal concentration for humans, in some cases, is not lethal for other organisms and vice versa. There is also a problem with standardizing test conditions. Several factors such as environmental stress (field testing during a hot or cold day) and additive effects of other compounds present may alter the toxic effects of Class A poisons on the test organisms.

This approach would indicate the presence of potentially lethal wastes but would not be confined to the sixteen Class A poisons of interest in this study. Additionally, the selection of quantities of sample for exposure and duration of the test creates an extremely complex problem, especially when the material to be tested is a complete unknown. An arbitrary definition would have to be established in which Class A poisons would be materials which produced the death of test organisms after a predetermined set concentration and time interval. Finally, some Class A poisons such as nitrous fumes exhibit a delay from the time of exposure to the onset of symptoms. This time delay would not be conducive for a rapid field screening test.

It would appear that any usefulness for this approach would be directed toward a general screening procedure for all toxic compounds. An example of such a screening aproach is DOT's white laboratory rat testing for determination of Class B poisons. This method, found in section 173.343 of Title 49 of the Code of Federal Regulations, lists specific procedures to follow for oral, inhalation and skin absorption toxicity. However, the time interval for these three types of tests is 48 hours and the test is conducted within a laboratory setting. This time factor is hardly conducive to rapid field screening of hazardous wastes at remote locations.

ENZYME TESTS

The use of enzymes as an indicator of Class A poisons was considered during this project. The enzyme approach involves selecting an enzyme that, when introduced to a specific compound or class of compounds, becomes inhibited to produce a specific end product. The detection capability of this system utilizes the production (or lack of production) of this specific end product, which is produced by the catalytic action of the enzyme. Colorimetric reactions can then be used to detect the presence of this end product.

An enzyme's ability to function as a catalyst is dependent upon two critical factors: (1) that the enzyme is not complexed with another compound, and (2) the structural integrity of the enzyme is maintained. If either of these cases occurs, the enzyme becomes deactivated and the end product is not produced.

The use of the enzyme cholinesterase as a detection device for nerve agents, and organophosphate and carbamate pesticides has been widely researched. Enzyme tickets for the detection of cholinesterase inhibitors are presently marketed for water and air analysis. In addition, the enzymes hexokinase and carbonic anhydrase have been researched for the detection of several chlorinated hydrocarbons and inorganic substances, such as pentachlorophenol, DDT, chlordane, and cyanide. Tables 7 and 8 illustrate the inhibition of these enzymes caused by the tested compounds at varying concentrations. It should be noted that the research was conducted for use with relatively clean aqueous matrices.

Our literature survey did not find research that had been conducted testing enzymes with Class A poisons in complex matrices. It became apparent

TABLE 7. INHIBITION OF CARBONIC ANHYDRASE[18]

Test compound	Grade purity	% Inhibition at several concentrations[a/]			
		10^{-4} M	$5x10^{-5}$ M	10^{-5} M	10^{-6} M
DDT relatives:					
DDT	Anal. std.[b/] 100%	34	29	11	--
DDT	Anal. std. 97%	28	28	5	--
Methoxychlor	Commercial 90%	40	25	55	--
Chlorophenoxy compounds:					
2,4,5,-T acids	Anal. std. 99%	+6	9	7	--
2,4,5-T butylesters	Anal. std. 100%	21	26	13	--
Aldrin-toxaphene group (toxaphene family):					
Toxaphene	Anal. std. 100%	44	39	3	--
Highly halogenated aromatics:					
Pentachlorophenol	Commercial 34%	70	72	12	--
2,4,5-Tri-chlorophenol	Anal. std. 98%	35	21	8	--
Cyanide compounds:					
Potassium cyanide	Reagent	100	--	100	46
Sodium cyanide	Reagent	100	--	79	21
Mercury compounds:					
Mercuric chloride	Reagent	100	--	55	0
Cadmium compounds:					
Cadmium chloride	Reagent	21	--	--	--

a/ Percentage depression in the activity of a standard enzyme solution.
b/ Anal. std. - Analytical standards received from EPA Pesticide and Toxic Substances Effects Laboratory, Research Triangle Park, North Carolina.

TABLE 8. INHIBITION OF HEXOKINASE[18]

Test compound	% Inhibition at several concentrations[a/]		
	3×10^{-4} M	10^{-4} M	10^{-5} M
Chlorinated hydrocarbons:			
Aldrin	55	17	--
Chlordane	92	22,60[b/]	--
DDD	0	--	--
DDT	93	40	61[b/]
Endosulfan	54	59	--
Heptachlor	--	40	40[b/,c/]
Lindane	100	49	55[b/]
Methoxychlor	100	26	--
Pentachlorophenol	0	--	--
Toxaphene	100	52	100[b/,c/]
Trichlorophenol	26	5,68[b/]	--
2,4,5-T acid	24	--	--
Organophosphates:			
DDVP	23	--	--
Dursban	17	--	--
Naled	22	--	--
Parathion	--	12	--
Carbamates:			
Furadan	15	--	--
Inorganic Ions:			
Strontium	0	--	--
Cadmium	--	38	--
Cyanide	--	6	--
Mercury	95	77	63[b/]
Aryl Phosphates:			
Phenylphosphate, disodium salt	13	--	--
Tri-o-cresyl phosphate	50-90	34	--
Tricresylphosphate (mixed cresols)	--	29	--

a/ Percent inhibition was calculated by assigning 100% activity to a dioxane control containing no test compound.

b/ Value was obtained using a modification of the test procedure given in this report. Glucose is added after inhibitor and enzyme are incubated for 5 min. This procedure increases the sensitivity to inhibition.

c/ Concentration was 2×10^{-5} M.

that enzyme techniques for the detection of various hazardous substances is at a developmental stage in comparison to other more traditional detection techniques such as colorimetric tests, photometric reactions, or gas chromatography. In addition, little work has been performed to determine what effects various matrices, other than water or air, can have on an enzyme's activity. It is known that organic solvents, even at less than 10 percent by volume,can inhibit an enzyme's activity. When screening a waste for Class A poisons, an operator would not necessarily know what type of matrix is present and therefore not be able to distinguish whether a decrease in the enzyme's activity was due to a Class A poison or occurred because of the matrix of the sample.

An alternative technique that may be feasible would be to strip the liquid sample of its volatile components using air and then place the enzyme on a solid support in the vapor generated by stripping. The effect of any non-volatile in the liquid sample should then be minimized. We could not locate any data using this technique for screening hazardous substances in an organic solvent matrix. Whether this technique would lower the concentration of the organic solvent to a level which would not interfere with an enzyme while still allowing detection of the substance in question is unknown. Basic research would have to be conducted in order to establish the validity of this approach.

A decision as to whether an enzyme approach is feasible for Class A poison detection can not be made without experimentation because of the lack of information on the enzyme ticket technique for specific Class A poisons and the possibility of matrix interaction. For this reason, enzyme techniques were not selected as one of the most promising approaches. However, a basic research effort to determine the feasibility of the stripping technique would certainly appear justified.

GENERAL SCREENING METHODS SUMMARY

The current state-of-the-art of existing general screening methods is neither practical nor feasible for the rapid field screening of unknowns at hazardous waste sites. The complexities of possible matricies and test conditions rule out many of the current general approaches. Two techniques, the Microtox™ Toxicity Monitor and the use of various enzymes, appear to offer many advantages for detecting toxic materials. Unfortunately, both of these methods are at a developmental stage. Further laboratory investigation using these systems appears to be worthwhile for general screening purposes. It must be noted that these two methods, if developed, would not be restricted in their detection capabilities to the sixteen Class A poisons of interest to this program. Instead, the relative degree of toxicity of the unknown would be assessed. It would appear that the Microtox™ Toxicity Monitor would offer more advantages than the enzyme ticket approach for general screening purposes if the Microtox™ response factor between very toxic and slightly toxic substances could be sufficiently attenuated to reflect the differences. This would necessitate an in depth laboratory evaluation of the Microtox™ Toxicity Monitor, possibly coupled with a novel sample preparation methodology.

As previously stated, the infrared analyzer may be useful as a technique for establishing the absence of specific Class A poisons in an unknown. This would aid greatly in reducing the number of individual tests for specific Class A poisons that might otherwise be required. Interferences would probably preclude the use of this technique as a positive confirmation of a specific Class A poison.

SECTION 6

SPECIFIC SCREENING METHODS FOR CLASS A POISONS

Current state-of-the-art technology suggests that no general field method is available which could be used to screen for Class A poisons in all types of sample matrices. Therefore, a literature survey was undertaken to determine candidate screening methods that might be used in the field for the detection of specific Class A poisons. The literature reviewed included the methods currently available from commercial sources, as well as general colorimetric and titrimetric assay methods published in the open literature. The intent of this literature review was to aid in the selection of the best candidate methods for use in screening for the Class A poisons of interest to this program. The purpose of this review was not to order all of the identified methods according to their relative usefulness but to select the two or three outstanding candidate methods for each Class A poison.

SEARCH STRATEGY

Three major sources of information were utilized in the literature search:

Manufacturers' Literature

Three manufacturers were found to be primary suppliers of test methods for many of the species of interest to this program.

- Dragerwork AG Lubeck, Federal Republic of Germany
- Matheson-Kitagawa, Bridgeport, NJ
- Mine Safety Appliances Company, Pittsburg, PA

The test methods offered by the above manufacturers consist of colorimetric detection tubes which are used to sample gases or vapors for specific substances.

Computerized Data Bases

Various computerized data files were searched in order to rapidly provide the most current information available on detection methods adaptable to field use. All Class A poisons were included in this search. The computer files consulted included, but were not limited to, the following: Chemical Abstracts Condensate: 1967 to present; Chemical Industry Notes: 1974 to present; National Technical Information Service: 1964 to present; Predicasts Overview of Markets and Technology: 1972 to present; and Toxicity Data Bank. Primary key words used during these searches were:

Colorimetric

Spectrophotometric

Titrimetric

Volumetric

Spot test(s)

Detection

Production

Collections of Analytical Methods

Various compilations of analytical methods were also consulted in order to include test methods found in the older technical literature. Primary sources of this information were:

Standard Methods for the Examination of Water and Wastewater[19]

Handbook of Analytical Chemistry[20]

Spot Tests in Inorganic Analysis[21]

Organic Reagents for Metals[22]

Colorimetric Determination of Traces of Metals[23]

Organic Analytical Reagents[24]

Manual Literature Survey

Chemical abstracts were manually searched for analytical methods on each Class A poison between 1927 and 1967.

CRITERIA FOR METHODS EVALUATION

In selection of the most promising detection methods for hazardous waste screening, several criteria were considered.

Type of Method

Colorimetric spot tests using detector tubes, treated paper, or liquid reagents were of primary interest. This was because of their ease of operation, test time and the relative convenience they offer for field use. Various general screening methods were considered, such as titrimetric, portable G.C., and infrared analyzers. Due to the increased degree of operator skill required, length of time to conduct tests, and/or method complexities, these detection techniques were eliminated from consideration. Commercial methods were chosen over those in which detection devices had to be prepared. In the event that no commercial methods were available, first consideration was given to the procedure which appeared easiest to perform and appeared to be the most specific.

Field Requirements

The test methods selected are for use in field surroundings. Although some rudimentary lab capabilities may be available, it was desirable

that the detection devices be portable and not require any outside electrical support. In addition, disposability was another factor which was considered. The generation of large volumes of liquid or solid wastes, whether toxic or not, is obviously undesirable.

Another factor to be considered in regard to a field situation was the shelf-life of reagents used. Obviously, it is desirable in a field situation to use reagent solutions that are stable for as long a period as possible. In the case under consideration, however, it should be possible to use basic laboratory facilities to prepare reagent solutions at the time of use, if necessary. Of course, any solid reagent powders selected for inclusion in a detection method should be stable indefinitely.

Interferences and Sensitivities

Methods which had either few interferences, or gave procedures to eliminate interfering species, were considered to be most favorable for selection. In fact, methods which included interference elimination steps were given preference over simpler methods which were subject to interference by many species.

The screening methods identified, using the above approach along with a discussion of each Class A poison, are presented in Section 7 of this report.

SECTION 7

DISCUSSION OF CLASS A POISONS

The current state-of-the-art of existing general detection methods is not suitable for the rapid screening of Class A poisons at hazardous waste sites. Therefore, it appears that a specific detection method for each of the Class A poisons of interest to this study is the more promising approach. A convenient method for the field screening of specific volatile substances is the use of gas detector tubes. Gas detector tubes are small cylindrical glass tubes (≈6.4 mm O.D. x 15.2 cm L) which contain a reagent that is specific for the gas or vapor for which the detection tube is designed. The reagent is supported on a solid substrate such as silica gel. Generally the front part of the detection tube, where the sample enters, contains chemicals which scrub out potentially interfering species before they reach the detection region of the tube. When a standard volume of sample, containing the species the detection tube is designed to measure, is drawn through the tube the reagent changes color. The length of this color change in the tube is indicative of the concentration of the substance in the sample. Samples to be analyzed are drawn through the gas detection tube at a fixed and reproducible rate using a small vacuum pump. The pump can be either electrically or hand operated; the rate is usually controlled using a limiting micro-orifice. The volume is controlled by counting the number of strokes made by the pump and multiplying by the gas volume drawn through the detection tube on each pump stroke.

Most tubes employ the traditional reference calibration chart, found on the inside of each detector tube box. The alternate method uses direct-reading tubes having the calibration scale printed directly on the tube. Both calibrations are based on a specific gas volume (number of pump strokes) being drawn through the detection tube. Once a sample is taken the length of stain in the detection tube is compared to the calibration chart or read directly from the scale on the detection tube.

The following subsections describe each of the Class A poisons including their physical, chemical and toxicological properties. Page ix may be consulted for definitions of abbreviations used in the toxicology tables. Also included are the candidate detecting reagents, their toxicity and relative cost. Particular attention was given to those methods which appeared adaptable to the gas detection tube approach described above.

ARSINE

The physical and chemical properties of arsine are given in Table 9. Also included in this table are data pertaining to the toxicological

properties of arsine as well as to its manufacture. Table 10 contains a summary of information concerning each of the detection reagent systems. The toxicity and price of each reagent system are given in Table 11. Each of the detection reagent systems is discussed in detail in the following sections.

Arsine Detection Reagent Recommendations

There are three commercially available colorimetric detection methods for arsine (Methods 10, 11 and 12) which appear to be the most promising candidates. Of the three methods, the Draeger Tube (Method 10) appears to offer advantages in selectivity in that a precleanse layer has been incorporated to eliminate certain interferences. The magnitude of the interferences that the precleanse layer will remove was not given in the literature and will have to be evaluated in the laboratory. Method 11 also appears to be a promising candidate, but a precleanse material such as used in Method 12 needs to be utilized in order to eliminate interferences. Method 12, which uses a commercially available kit, might be worthy of investigation if the other two methods mentioned above cannot be made to work satisfactorily.

TABLE 9. PROPERTIES OF ARSINE[3,4,25,26,27]

NAME OF SUBSTANCE:	Arsine
MOLECULAR FORMULA:	AsH_3
MOLECULAR WEIGHT:	77.93
CAS REGISTRY NUMBER:	7784-42-1
WISWESSER LINE NOTATION:	As H_3
SYNONYMS:	A. Arsenic hydride B. Arsenic trihydride C. Arseniuretted hydrogen D. Arsenous hydride E. Hydrogen arsenide F. Arsendwodor (Polish) G. Arsenwasserstoff (German)
MELTING POINT:	-116.3°C
BOILING POINT:	-55°C
DENSITY/SPEC GRAVITY:	3.484 g/l
VAPOR PRESSURE:	760 mm Hg at -55°C
COLOR/FORM:	Colorless gas
SOLUBILITY:	A. Slightly soluble in ethyl alcohol, alkalies B. 20 ml in 100 ml of water at 24°C
STABILITY/SHELF LIFE:	A. Decomp. when heated. B. On exposure to light, moist arsine decomp. quickly, depositing shiny black arsenic.
EXPLOSIVE LIMITS:	A. Moderate when exposed to flame. B. Reacts vigorously with oxidizing materials.
MAJOR USES:	Doping gas used in mfr. of integrated circuits.
SPECTRAL AND OTHER PROPERTIES:	A. Odor resembling onions or carbide B. Vapor density: 2.66 g/l

(continued)

TABLE 9 (continued)

C. Dissociation pressure @ °C: 0.806 atm.

D. Aqueous solutions are neutral.

TOXCITY VALUES:

A. TC_{Lo} Human inhalation 230 gm/m^3: TFX: SYS

B. TC_{Lo} Human inhalation 9.75 mg/m^3: TFX: RBC

C. LC_{50} Human inhalation 81.25 mg/m^3 for 30 min.

D. LC_{Lo} Rat inhalation 300 mg/m^3 for 15 min.

E. LD_{Lo} Mouse inhalation 70 mg/m^3 for 3 hrs.

F. LC_{Lo} Dog inhalation 400 mg/m^3 for 15 min.

G. LC_{Lo} Rabbit inhalation 500 mg/m^3 for 15 min.

H. LD_{Lo} Frog inhalation 4500 mg/m^3 for 3 hrs.

I. Toxic hazard ratings: acute local: inhalation 3; acute systemic: inhalation 3; chronic systemic: inhalation 3. 3= high: may cause death or permanent injury after very short exposure to small quantities.

THRESHOLD LIMIT VALUE: 0.16 mg/m^3

PHYSIOLOGICAL EFFECTS:

A. Symptoms of poisoning may appear within an hr. or two of the causal exposure.

B. Headache, dizziness, nausea, epigastric pain.

C. Jaundice

D. Weakness

MANUFACTURING INFO:

A. By reduction of arsenic compound. This is usually affected by nascent hydrogen produced by the action of dilute mineral or other acids on certain metals in presence of compound of arsenic.

B. By hydrolysis of certain metallic arsenides such as those of sodium, zinc and aluminum. Such arsenides may be produced as a side reaction of some other indust. chemical process.

PRODUCTION: No information available

MANUFACTURERS:

A. Airco, Inc. Airco Indust Gases Div., Santa Clara, CA.

B. G. D. Searle & Co., Will Ross, Inc., Subsid. Matheson Gas Products, Div., Cucamonga, CA, East Rutherford, NJ.

(continued)

TABLE 9 (continued)

ENVIRONMENTAL HAZARDS:	A.	Odor cannot be relied upon for detection.
	B.	Wear gastight chemical safety goggles and respiratory protective equipment.

TABLE 10. ARSINE DETECTING REAGENTS

Reagents	Method Matrix	Interferences	Sample Type of Matrix	Sensitivity	# of Operator Steps	Ref No.
1. Silver diethyldithiocarbonate	photometric	Sb	air	1 ug (As)	3, exp. operator	19
2. Mercuric bromide stain	test paper	Sb	air	0-30 mg (As)	3, exp. oper. 1-1/2 hr.	19
3. Sodium p-argentosulfamidobenzoate	photometric		liquid or air	0.1 to 8 mg/ml (As)	3	28
4. Silver sulfanilamide	photometric		liquid or air	Not Available	3	29
5. Mercuric chloride	test paper	H_2S*	air	> 310 mg/m^3	2	30
6 Auric chloride; Mercuric chloride	silica gel	H_2S*	air	Not Available	2	31
7. Silver fluoride	silica gel	Sb	air	0.16 mg/m^3	2	32
8. Silver nitrate; Nitric acid	test paper	H_2S*, Sb	air	> 310 mg/m^3	2	33
9. Bromine; Methyl red	titration	Any substance that reacts w/t Br_2	liquid or air	10^{-4}M	numerous	34
10. Draeger detection tube	silica gel	Phosphine, Antimony hydride	gas	0.2 mg/m^3	1	35
11. Matheson-Kitagawa detection tube	silica gel	Hydrogen selenide, Phosphine	gas	16.25 mg/m^3	1	36
12. MSA arsine reagent kit	photometric	Stibine, Phosphine	gas	0.08 mg/m^3	2	37

TABLE 11. TOXICITY AND COST OF ARSINE DETECTING REAGENTS

Reagents	Toxicity - Acute Local[3]	Cost $[38,39,40]
1. Silver diethyldithiocarbonate	Unknown	No Firm Price Quoted
2. Mercuric bromide	Irritant-3; Ingestion 3; Inhalation 2	100g - 18.55
3. Sodium p-argentosulfamidobenzoate	Unknown	not readily available from sources checked
4. Silver sulfanilamide	Unknown	Not readily available from sources checked
5. Mercuric chloride	Chlorides-Variable;Mercury Compounds-Irritant-3; Ingestion 3; Inhalation 3	100g - 40.25
6. Auric chloride; Mercuric chloride	Chlorides-Variables; Gold Compounds-Allergen 2; Mercury Compounds-Irritant 3; Ingestion 3; Inhalation 3	1g - 23.00; 100g - 40.25
7. Silver fluoride	Fluorides-Irritant 3; Ingestion 3; Inhalation 3	10g - 35.00
8. Silver nitrate; Nitric acid	Nitrates-Ingestion 2; Inhalation 2	10g - 30.00
9. Bromine; Methyl red	Irritant 3; Ingestion 3; Inhalation 3-Bromine	50ml - 56.00; 10g - 10.50
10. Draeger detection tube	None - Closed tube	1.00 to 2.00 per tube

0 NONE: (a) No harm under any conditions: (b) Harmful only under unusual conditions or overwhelming dosage.

1 SLIGHT: Causes readily reversible changes which disappear after end of exposure.

2 MODERATE: May involve both irreversible and reversible changes not severe enough to cause death or permanent injury.

3 HIGH: May cause death or permanent injury after very short term exposure to small quantities.

U Unknown-No valid information available on Humans

(continued)

TABLE 11 (continued)

Reagents	Toxicity - Acute Local	Cost $[38,39,40]
11. Matheson-Kitagawa detection tube	None - Closed tube	1.00 to 2.00 per tube
12. MSA Arsine reagent kit	Unknown	50.00

0 NONE: (a) No harm under any conditions: (b) Harmful only under unusual conditions or overwhelming dosage.

1 SLIGHT: Causes readily reversible changes which disappear after end of exposure.

2 MODERATE: May involve both irreversible and reversible changes not severe enough to cause death or permanent injury.

3 HIGH: May cause death or permanent injury after very short term exposure to small quantities.

U Unknown-No valid information available on Humans

(1) Silver Diethyldithiocarbonate [19] - This method involves passing arsine through a scrubber containing glass wool impregnated with lead acetate solution and then into an absorber tube containing silver diethyldithiocarbonate dissolved in pyridine. In the absorber arsenic reacts with the silver salt to form a soluble red complex that is then measured photometrically. This procedure can detect as little as 1 mg (as As) of arsine. The disadvantages of this method is that antimony acts as an interference and successful application of the method often requires an experienced operator. In addition the reagent is dissolved in pyridine, a very flammable liquid, and emits cyanide gases upon decomposition. This method does not appear to be as promising as other detection means for arsine.

(2) Mercuric Bromide Stain Method [19] - For this method arsine is passed through a column containing lead acetate solution. The arsine produces a yellow-brown stain on test paper strips of mercuric bromide. The length of the stain is thought to be roughly proportional to the concentration of arsine present. This method can detect from 0-30 mg Arsine as (As). Antimony again interferes with this test and the time involved is an hour and a half. Therefore, this method does not appear to be viable for field use.

(3) Sodium p-Argentosulfamidobenzoate [28] - Arsine is reacted with sodium p-argentosulfamidobenzoate in the presence of piperazine to form a stable silver solution. This solution is then examined spectrometrically to determine the arsenic content. The range of this procedure is 0.1 to 8 mg As/ml. This method does not have the advantages of other colorimetric tests available in which direct readings can be conducted on filter paper or detector tubes. The reagent for this test is also not a readily available commercial item. Due to these reasons, we do not recommend further investigation of this approach.

(4) Silver Sulfanilamide [29] - The procedure is similar to the previous method in that arsine is absorbed in alkaline silver sulfanilamide to form the stable silver which is measured spectrometrically. This approach has the same disadvantages of the previous method and is not as sensitive. Therefore, we do not recommend this procedure as being one of the most promising detection methods for arsine.

(5) Mercuric Chloride [30] - This method consists of drawing air through filter paper that has been impregnated with mercuric chloride solution. The color intensity of the stain is then compared to those obtained with known standard quantities of arsine. This procedure is not as sensitive as the combined mercuric chloride - auric chloride method. Due to its lack of

sensitivity in comparison to other similar techniques, this procedure does not warrant further consideration.

(6) Auric Chloride and Mercuric Chloride [31] - This technique involves impregnating silica gel with a solution containing 0.25g of gold chloride, 0.16g mercury chloride, 0.34ml of concentrated hydrochloric acid, and 25ml of water. It is also advisable to superimpose a granular layer containing lead acetate to eliminate errors due to the presence of hydrogen sulfide in the gases to be tested. While each of these two reagents will detect arsine separately, the combination of the two greatly increases sensitivity. This method, devised by Draeger, probably contains the same reagents found in the commercially available Draeger tube. Therefore, this method will be considered in the same manner as the Draeger tube method for arsine detection.

(7) Silver Fluoride [32] - For the detection of arsine, 3 g of silica gel are impregnated with 1ml of 25 percent silver fluoride solution. To detect arsine, at approximately 0.16 mg/m^3, the reagent is exposed for 10 minutes at 100 liters of air per minute. The gel color is then compared to known standards. Stibine interferes with this test. This procedure involves preparing a detector tube. Therefore, this method will be considered for further investigation only if currently pre-made detection tubes/kits prove unsatisfactory.

(8) Silver Nitrate and Nitric Acid [33] - Filter paper is impregnated with silver nitrate and nitric acid. This paper is placed in a tube behind papers impregnated with lead acetate to remove hydrogen sulfide. Air samples are then drawn through the tube and the resulting color change on the filter paper indicates the presence of arsine. This method appears to have been developed for sampling relatively clean matrices. It would appear that in sampling hazardous wastes too many potential interferences would be encountered to make this a viable approach.

(9) Bromine and Methyl Red [34] - This method is based upon the premise that arsenic gases react rapidly with bromine, a reagent which allows very accurate titrations in dilute solutions. A sample (1 to 5ml) is placed in a test tube and adjusted to 0.1 M sulfuric acid by addition of a few drops of concentrated sulfuric acid. One drop of methyl red is added for each ml of solution. Dilute (10^{-4} M) bromine solution is then added until the solution becomes nearly colorless. Another drop of methyl red is introduced and bromine added until the sample becomes colorless.

This procedure does not appear suitable for field use for a variety of reasons. It is necessary to standardize the dilute bromine solution prior to use on account of a possible 10 to 30 percent loss in strength due to the potential presence of reducing agents. In addition, the endpoint of the procedure is not reversible so care must be taken not to over titrate. Any compound that reacts with bromine will interfere with the titration, so the procedure has numerous interferences. Finally, procedures involving titrations are time consuming, cumbersome, and require a degree of expertise to obtain reliable results. Because of these factors, we do not believe that this method warrants any further consideration.

(10) Draeger (No. CH25001) [35] - Draeger offers a gas detector tube which can detect arsine in the concentration range of 0.16 to 9.75 mg/m^3 using a 20 stroke (2000 ml) sample. The potentially interfering gases (hydrogen sulfide, hydrogen selenide, mercaptans, ammonia, and hydrogen chloride) are retained in a pre-cleanse layer. The relative standard deviation of this detector tube for arsine is 20 to 15 percent depending on arsine concentration. Phosphine and antimony hydride are considered to be interferences with this tube but generally produce a minimal response. The Draeger detection tube for arsine has a known shelf life of approximately two years. It would appear that this detection tube is a good candidate for the detection of arsine at hazardous waste sites.

(11) Matheson-Kitagawa (No. 140) [36] - Matheson markets a gas detector tube for the measurement of arsine. The measurable concentration range of the tube is 16.25-520 mg/m^3 using one pump stroke (100 ml). Hydrogen selenide/hydrogen sulfide and phosphine are interferences in the presence of this tube.

This method is considered to be an alternate to method 10. It does not offer the sensitivity or pre-cleanse layer of the preceding technique but may be modified in the laboratory to overcome these deficiencies.

(12) MSA (Nos. 81101 and 81220) [37] - MSA does not have an arsine gas detector tube but they do supply an arsine reagent kit which can be used with the MSA sample pump. An additional accessory kit is also required in order to eliminate hydrogen sulfide and sulfur dioxide interference. The measurable concentration range for arsine using MSA's reagent kit is 0.81 to 3.25 mg/m^3. Stibine and phosphine are still considered to be positive interferences even with the interference removal accessory kit. This kit, while commercially available, does not appear to offer the advantages of operation and specificity of the colorimetric detection tubes.

BROMOACETONE

This compound was developed by the Germans in an attempt to discover toxic war gases. Only four reagent systems were located which dealt with the detection of bromoacetone. Table 12 lists various data pertaining to bromoacetone while Tables 13 and 14 contain a summary of information pertaining to each of the four detection reagent systems. Each of the detection reagent systems are discussed in detail in the following sections.

Bromoacetone Detection Reagent Recommendations

There are no commercially available test kits available for the detection of bromoacetone. In addition, it appears that none of the four listed reagent systems is sufficiently specific to detect this compound confidently without the possibility of false positive results. Therefore, it is recommended that a two-step detection process be used to determine the presence of bromoacetone. The fuchsin - sulfur dioxide method would first be used to establish the presence of bromine. If this test is positive, the sodium nitroprusside test would be conducted to also establish the presence of the carbonyl group. A positive result for both tests would strongly suggest the presence of bromoacetone. Colorimetric detection tubes are available which could possibly be used to establish the presence of the carbonyl group in bromoacetone.

TABLE 12. PROPERTIES OF BROMOACETONE[3,4,25,26,27]

NAME OF SUBSTANCE:	Bromoacetone
MOLECULAR FORMULA:	C_3H_5BrO
MOLECULAR WEIGHT:	136.98
CAS REGISTRY NUMBER:	598-31-2
WISWESSER LINE NOTATION:	E1V1
SYNONYMS:	A. Bromoacetone B. Bromo-2-propanone C. 1-Bromo-2-propanone D. Acetonyl bromide E. Acetylmethyl bromide
MELTING POINT:	-36.6°C
BOILING POINTS:	136.5°C @ 725 mm Hg
DENSITY/SPEC GRAVITY:	1.634 g/l @ 23°C
VAPOR PRESSURE:	9 mm Hg @ 20°C
COLOR/FORM:	A. Colorless when pure, but turns purple B. Liquid
SOLUBILITY:	A. Slightly soluble in water B. Soluble in alcohol C. Soluble in ether D. Soluble in acetone
STABILITY/SHELF LIFE:	Turns violet rapidly, even in absence of air. Keep tightly closed & protected from light.
EXPLOSIVE LIMITS:	No information available
MAJOR USES:	A. Tear gas B. Used in organic synthesis C. Chemical war gas

(continued)

TABLE 12 (continued)

SPECTRAL AND OTHER PROPERTIES:	A. Sadtler reference number: 16158 (IR, PRISM) B. Partial decomposition at boiling point C. Vapor density: 4.75 g/l D. Index of refraction: 1.4697 @ 15°C/D E. Pungent odor
TOXCITY VALUES:	A. LC_{Lo} Mice inhalation 600 mg/m^3 B. Aquatic toxicity: TLm: 56-560 mg/m^3/96 hr C. LC_{Lo} Human inhalation 3203 mg/m^3/10 minutes D. Toxic hazard rating: acute local: irritant 3; inhalation 3. 3=high: may cause death or permanent injury after very short exposure to small quantities. E. Dangerous when strongly heated, emits highly toxic fumes.
THRESHOLD LIMIT VALUE:	No information available
PHYSIOLOGICAL EFFECTS:	A. Intensely irritating to the skin and mucous membranes. B. Powerful lacrimator.
MANUFACTURING INFO:	A. Prepared by bromination of acetone, and by bromination of acetone enol acetate. B. Produced by treating aqueous acetone with bromine & sodium chlorate @ 30-40°C.
PRODUCTION:	No information available
MANUFACTURERS:	No information available
ENVIRONMENTAL HAZARDS:	Personnel exposed to its vapors should wear gastight chemical safety goggles and respiratory protective equipment. Whenever possible, this material should be used in enclosed systems.

TABLE 13. BROMOACETONE DETECTING REAGENTS

Reagents	Method Matrix	Interferences	Sample Type of Matrix	Sensitivity	# of Operator Steps	Ref No.
1. Sodium nitroprusside	colorimetric	Any active methylene group	air	Not Available	3	41
2. Fluorescein	paper-colorimetric	Any bromine Sub.	liquid or air	Not Available	2	42
3. Ammoniacal silver nitrate	precip.	Lewisite, Bromo-Benzylcyanide, & Chloroacetophenone	liquid or air	560 mg/m^3	2	43
4. Fuchsin; Sulfur dioxide	paper-colorimetric	Possibly other bromo type compounds	air	Not Available	2	43

TABLE 14. TOXICITY AND COST OF BROMOACETONE DETECTING REAGENTS

Reagents	Toxicity - Acute Local[3]	Cost - $[38,39,40]
1. Sodium nitroprusside	Unknown	100g - 17.00
2. Fluorescein	Allergen 1	100g - 5.05
3. Ammoniacal silver nitrate	Nitrates - Ingestion 2, Inhalation 2 Irritation 3, Inhalation 2, Irritant 2	10g - 30.00; 500ml-6.65
4. Fuchsin; Sulfur dioxide	Possible Carcinogen; Irritant 3; Ingestion 3, Inhalation 3	25g - 14.00; 250g - 13.50

0 NONE: (a) No harm under any conditions: (b) Harmful only under unusual conditions or overwhelming dosage.

1 SLIGHT: Causes readily reversible changes which disappear after end of exposure.

2 MODERATE: May involve both irreversible and reversible changes not severe enough to cause death or permanent injury.

3 HIGH: May cause death or permanent injury after very short term exposure to small quantities.

U Unknown-No valid information available on Humans

(1) Sodium Nitroprusside [41] - This technique involves passing a gas sample through a warm, alcoholic, 0.5 N potassium hydroxide solution. A few drops of sodium nitroprusside solution is then added to the first solution. If bromoacetone is present, a red coloring will be produced which can be intensified by the addition of acetic acid to form a pink-violet coloration.

The basis of the color reaction is that the nitric oxide group of the nitroprusside reacts with acetone to give isonitroso-acetone, which remains in the complex anion, while the iron becomes reduced. Methyl ketones and compounds which contain an enolizable caron monoxide group give similar color reactions. In addition, aldehydes, alkali sulfides, zinc and sulfur dioxide will act as interferences.

This test may be used in conjunction with method 4 to establish the probable presence of bromoacetone.

(2) Fluorescein [42] - Bromoacetone is adsorbed by activated carbon and is then oxidized. Bromine is then liberated by blowing a stream of air through the carbon. The presence of cyanide, chloropicrin and chlorine do not inhibit the reaction unless the latter is present in great excess. In the presence of iodine, the pink coloration of the eosin formed often changes color, but can be restored if exposed to ammonia fumes.

(3) Ammoniacal Silver Nitrate [43] - This procedure involves adsorbing a gas sample on silica gel. A piece of this gel is then placed in a test tube containing 5 percent silver nitrate solution to which a quarter of the volume of 10 percent ammonia has been added. The solution is clear at first, but, in the presence of bromoacetone, silver is precipitated and both granules and solution darken. This technique is sensitive at concentrations of less than 0.01 percent bromoacetone. This reaction is also given by chloroacetophenone, bromobenzyl cyanide and lewisite.

The silver nitrate procedure does not appear to be one of the most promising techniques due to its susceptibility to interference problems. We will not consider this approach as an alternative candidate for laboratory evaluation.

(4) Fuchsin - Sulfur Dioxide [43] - This technique involves treating a piece of filter paper with 0.1 percent fuchsin in water; 5 percent sodium bisulfite solution is added dropwise, just until decolorization occurs. Damp paper used will give a violet color in the presence of bromine. Chlorine will not interfere with this reaction but other bromo-containing compounds may. This method may be adaptable to the colorimetric detection tube approach.

CYANOGEN

The literature search for the detection of cyanogen was not very informative. Only a few reagent systems were reported which specified cyanogen detection. These detection reagent systems are discussed in detail in the following sections. Table 15 gives various information concerning cyanogen, while Tables 16 and 17 summarize each of the candidate detection reagent systems.

Cyanogen Detection Reagent Recommendations

There are no currently available commercial colorimetric detection methods for cyanogen. Of those reviewed, method one appears to be the most promising. However, considerable laboratory work is necessary to establish interference levels, if any, for cyanide compounds. If this method does not appear promising after initial laboratory evaluation, other screening tests for hydrocyanic acid and cyanogen chloride will be investigated for sensitivity to cyanogen.

TABLE 15. PROPERTIES OF CYANOGEN[3,4,25,26,27]

NAME OF SUBSTANCE:	Cyanogen
MOLECULAR FORMULA:	C_2N_2
MOLECULAR WEIGHT:	52.04
CAS REGISTY NUMBER:	460-19-5
WISWESSER LINE NOTATION:	NCCN
SYNONYMS:	A. Oxalonitrile B. Oxalic acid dinitrile C. Ethanedinitrile D. Dicyan E. Prussite F. Dicyanogen G. Oxalic acid dinitrile H. Carbon nitride I. Oxalyl cyanide J. Nitriloacetonitrile
MELTING POINT:	-27.9°C
BOILING POINT:	-21.17°C @ 760 mm Hg
DENSITY/SPEC GRAVITY:	0.9537 g/l @ -21°C @ 4°C
VAPOR PRESSURE:	760 mm Hg at -21.17°C
COLOR/FORM:	Colorless gas
SOLUBILITY:	A. One volume of water dissolves about 4 volumes of cyanogen gas B. Soluble in ethyl alcohol: 2300 ml/100 ml alcohol @ 20°C C. Soluble in ether: solubility in ethyl ether: 500 ml/100 ml ether @ 20°C D. Soluble in acetic acid
STABILITY/SHELF LIFE:	A. Above 500°C polymerizes into insoluble paracyanogen (CN)N

(continued)

TABLE 15 (continued)

B. Aqueous solution slowly decomp. to ammonium oxalate and formate, hydrogen cyanide, and urea

C. Slowly hydrolyzed in aqueous solution giving oxalic acid and ammonia

EXPLOSIVE LIMITS:

A. Upper-32% in air; lower-6% in air.

MAJOR USES:

A. Used as fumigant

B. Present in blast furnace gases

C. Organic synthesis

D. Fuel gas for welding and cutting heat-resistant metals

E. Rocket and missile propellant

SPECTRAL AND OTHER PROPERTIES:

A. Almond-like odor.

B. Acrid and pungent when in lethal concentration

C. Burns with pink flame having bluish border.

D. Heat of vaporization (liquid): 5.778 kcal/mol

E. Vapor density: 1.8 g/l

F. Max absorption (gas): 219 nm

G. Mg/l is equiv to 469.6 ppm and 1 ppm is equiv. to 2.127 mg/m^3 @ 25°C, 760 mm Hg

H. With oxygen it gives hottest flame known

TOXICITY VALUES:

A. LC_{Lo} Mice inhalation 740 mg/m^3

B. LC_{50} Rats inhalation 744 mg/m^3/1 hr

C. LC_{Lo} Cats inhalation 208 mg/m^3

D. LC_{Lo} Rabbits inhalation 804 mg/m^3

E. LD_{Lo} Rabbits subcutaneous 18 mg/kg

F. LD_{Lo} Frogs subcutaneous 43 mg/kg

G. TD_{Lo} Human inhalation 34 mg/m^3

H. Volatile cyanides resemble hydrocyanic acid physiologically, inhibiting tissue oxidation and causing death through asphyxia. Cyanogen is probably as toxic as hydrocyanic acid.

(continued)

TABLE 15 (continued)

I. Acute local: irritant 1. chronic systemic: ingestion 1; inhalation 1. 1=slight: causes readily reversible changes which disappear after end of exposure. (Cyanides)

J. Chronic local: irritant 2. 2=moderate: may involve both irreversible and reversible changes not severe enough to cause death or permanent injury. (Cyanides)

K. Acute systemic: ingestion 3; inhalation 3; skin absorption 3. 3=high: may cause death or permanent injury after very short exposure to small quantities. (Cyanides)

L. Adverse effects: death is asphyxial. Either circulation or respiration may fail first.

M. It hydrolyzes to yield 1 molecule of hydrogen cyanide (HCN) and one of cyanate. This is basis for supposition that cyanogen is comparable in toxicologic effect to hydrogen cyanide.

N. Dangerous when heated to decomposition or on contact with acid, acid fumes, water or steam; it will react to produce highly toxic fumes.

O. Rabbits showed practically no effect after 4 min exposure to 100 ppm (210 mg/m^3), slight symptoms after 4 hr exposure to 200 ppm (420 mg/m^3), severe symptoms and delayed death after 3.5 hr to 300 ppm (630 mg/m^3).

P. Mice recovered after 15 min exposure to 235 ppm (500 mg/m^3). Fatal response occurred after 12 min exposure to 2600 ppm (5500 mg/m^3) and after less than 1 min exposure to 15,000 ppm (31500mg/m^3).

THRESHOLD LIMIT VALUE: A. 10 ppm (approx. 22 mg/m^3).

PHYSIOLOGICAL EFFECTS: A. Workers who are daily exposed to cyanide solution may develop a "Cyanide" rash. Characterized by itching & by macular, papular & vesicular eruptions. Frequently there is secondary infection. (Cyanides)

MANUFACTURING INFO: A. Usually prepared by adding aqueous solution of sodium or potassium cyanide to aqueous solution of copper(II) sulfate or chloride.

(continued)

TABLE 15 (continued)

B. By heating mercury cyanide.

C. From hydrocyanic acid with use of copper oxide.

D. Alternate procedure for preparing $(CN)_2$ from HCN by use of CuO.

PRODUCTION: No information available

MANUFACTURERS: No information available

ENVIRONMENTAL HAZARDS: A. Firefighting method: the extinguishment of gas fires may be carried out with CO_2, dry chem, or in some cases, with water supply. Flammable within range of 6.60-42.60% by vol in air.

TABLE 16. CYANOGEN DETECTING REAGENTS

Reagents	Method Matrix	Interferences	Sample Type of Matrix	Sensitivity	# of Operator Steps	Ref No.
1. 8-Quinolinol; Potassium cyanide	colorimetric	specific	liquid or air	1 mg	2	44 45

TABLE 17. TOXICITY AND COST OF CYANOGEN DETECTING REAGENTS

Reagents	Toxicity - Acute Local[3]	Cost - $ [38,39,40]
1. 8-Quinolinol; Potassium cyanide	Details Unknown; Irritant 1, Ingestion 3	25g-4.40; 500g-15.00

0 NONE: (a) No harm under any conditions: (b) Harmful only under unusual conditions or overwhelming dosage.

1 SLIGHT: Causes readily reversible changes which disappear after end of exposure.

2 MODERATE: May involve both irreversible and reversible changes not severe enough to cause death or permanent injury.

3 HIGH: May cause death or permanent injury after very short term exposure to small quantities.

U Unknown-No valid information available on Humans

(1) 8-Quinolinol and Potassium Cyanide [44,45] - In this procedure, a paper is prepared by bathing it in a ten percent solution of 8-quinolinol in ether and drying in air. It has been stated that this reagent paper is stable. The paper is then moistened with a drop of 25 percent potassium cyanide solution. When the paper is exposed to cyanogen, an intense red stain will appear. Sensitivity is given as 1 mg of dicyanogen.

(2) The current listing of available gas detection tubes from Draeger, Matheson and MSA indicated that there currently is no gas detection tube available for the measurement of cyanogen. However, a listing January 1969 from MSA showed a gas detection tube #91624 for the measurement of cyanogen in the 4.25-213 mg/m^3 range. This detection tube required a pyrolyzer accessory. Listed interferences included hydrogen sulfide, halogen/nitrogen and hydrocarbon compounds. It appears that this tube, if available, would be subject to a wide variety of interferences.

(3) Other - The above methods were the only approaches, out of ten techniques reviewed, that specified cyanogen detection and that also appeared suitable for field screening. Other screening tests for cyanogen chloride and hydrocyanic acid were capable of detecting cyanogen, but were not mentioned as being specifically able to detect this substance. Laboratory investigation will be carried out in an attempt to discover which techniques for cyanogen chloride and hydrogen cyanide are able to detect cyanogen. Ruch, in Chemical Detection of Baseous Pollutant, p. 84, 1966, stated that most detection methods for cyanides are also sensitive to cyanogen.

CYANOGEN CHLORIDE

Seven methods were identified that could be used for the field detection of this gas. The physical, toxicological, manufacturing, and other various information concerning this substance are listed in Table 18. A description of the seven detection methods is given below, while Tables 19 and 20 contain data pertaining to each of the detection reagents.

Cyanogen Chloride Detection Reagent Recommendations

The apparent method of choice (Method 7) detecting cyanogen chloride appears to be the Draeger detector tube. This method is readily available with a known shelf life. Other reagent systems, described in the following sections, will be examined in the event that the Draeger tube performs unsatisfactory during laboratory testing. Specifically, Methods 1, 2 and 5 will be considered if Method 7 encounters unsolvable problems in the laboratory.

TABLE 18. PROPERTIES OF CYANOGEN CHLORIDE[3,4,25,26,27]

NAME OF SUBSTANCE:	Cyanogen chloride
MOLECULAR FORMULA:	CClN
MOLECULAR WEIGHT:	61.47
CAS REGISTRY NUMBER:	506-77-4
WISWESSER LINE NOTATION:	G CN
SYNONYMS:	A. Chlorocyanogen B. Chlorure de cyanogene (French) C. Chlorine cyanide D. CK E. Chlorocyanide F. Chlorocyan
MELTING POINT:	-6°C
BOILING POINT:	12.66°C @ 760 mm Hg
DENSITY/SPEC GRAVITY:	1.186 g/l @ 20°C/4°C
VAPOR PRESSURE:	1000 mm Hg @ 20°C
COLOR/FORM:	Colorless liquid or gas
SOLUBILITY:	A. Solubility in 100 ml of water: 2500 ml @ 20°C B. Solubility in 100 ml of ethanol: 10,000 ml @ 20°C C. Solubility in 100 ml of ether: 5000 ml @ 20°C D. Soluble in all organic solvents
STABILITY/SHELF LIFE:	Tends to form polymers on storage
EXPLOSIVE LIMITS:	No information available
MAJOR USES:	A. Chemical synthesis B. Military poison gas C. Insecticide

(continued)

TABLE 18 (continued)

SPECTRAL & OTHER PROPERTIES:	A. Vapor density: 2 g/l (air = 1)
	B. Conversion factors: 1 mg/l is equiv to 398 ppm & 1 ppm is equiv to 2.51 mg/m^3 @ 25°C, 760 mm Hg.
	C. Pungent odor detectable at 2.5 mg/m^3 (1 ppm).
TOXICITY VALUES:	A. LD_{50} Rats inhalation 296 mg/m^3/30 min
	B. LC_{50} Mice inhalation 294 mg/m^3/30 min
	C. LD_{Lo} Mice subcutaneous 39 mg/kg
	D. LC_{Lo} Dogs inhalation 198 mg/m^3/8 hr.
	E. LD_{Lo} Dogs subcutaneous 5 mg/kg
	F. LD_{50} Rabbits inhalation 520 mg/m^3/30 min.
	G. LD_{Lo} Rabbits subcutaneous 20 mg/kg
	H. LO_{50} Guinea pigs inhalation 520 mg/m^3/30 min.
	I. Aquatic toxicity: TLm: under 2.15 mg/m^3/96 hr.
	J. Lethal dose mice inhalation 1004 mg/m^3/3 min.
	K. Lethal dose rabbits inhalation 3012 mg/m^3/2 min.
	L. Lethal dose cats inhalation 100 mg/m^3/18 min. fatal after 9 days.
	M. Lethal dose cats inhalation 301 mg/m^3/3.5 min.
	N. Lethal dose cats inhalation 1004 mg/m^3/less than 1 min.
	O. Lethal dose dogs inhalation 120 mg/m^3/6 hr.
	P. Lethal dose dogs inhalation 803 mg/m^3/7.5 min.
	Q. Lethal dose goats inhalation 2510 mg/m^3/3 min fatal after 70 hrs.
	R. Lethal dose humans inhalation 399 mg/m^3/10 min.
	S. Lethal dose humans inhalation 108 mg/m^3/30 min.
	T. Toxic levels: in man inhalation of 50 mg/m^3(20 ppm) was intolerable after 1-min. exposure, 5 mg/m^3 (2 ppm) was intolerable after 10 min. exposure.
	U. Toxic levels: in man 2.5 mg/m^3 (1 ppm) was lowest irritant concn. after 10 min. inhalation exposure.

(continued)

TABLE 18 (continued)

V. Mice inhalation of 200 mg/m^3 (80 ppm) cyanogen chloride for 5 min. was tolerated by some animals; 300 mg/m^3 (120 ppm) for 3.5 min. was fatal to some animals.

W. Toxic hazard rating: acute local: irritant 1. Chronic systemic: ingestion 1; inhalation 1. 1=slight: causes readily reversible changes which disappear after end of exposure. (Cyanides)

X. Toxic hazard rating: acute local: irritant 3. Acute systemic: ingestion 3; inhalation 3. 3=high: may cause death or permanent injury after very short exposure to small quantities. (Hydrochloric acid)

Y. Toxic hazard rating: acute systemic: ingestion 3; inhalation 3; skin absorption 3. 3=high: may cause death or permanent injury after very short exposure to small quantities. (cyanides)

Z. Toxic hazard rating: chronic local: irritant 2. 2=moderate: may involve both irreversible and reversible changes; not severe enough to cause death or permanent injury. (Cyanides, Hydrochloric acid)

AA. TC_{Lo} Humans inhalation 10 mg/m^3. Exposure time not stated.

THRESHOLD LIMIT VALUE: No official TLV has been published. The value should certainly be less than 1.26 mg/m^3.

PHYSIOLOGICAL EFFECTS:

A. There is a combined effect of pulmonary edema and the interference of cellular metabolism by the cyanide radical.

B. Cyanogen chloride resembles the other cyanides in its action, but it is more irritating to the air passages & to the skin.

C. Toxicity: vapors are highly irritant & very poisonous.

D. Lacrimator

MANUFACTURING INFO.:

A. It is prepared by action of chlorine on hydrogen cyanide.

(continued)

TABLE 18 (continued)

B. Cyanogen chloride is produced by action of chlorine on moist sodium cyanide suspended in carbon tetrachloride & kept cooled to -3°C followed by distillation.

PRODUCTION: No information available

MANUFACTURERS: No information available

ENVIRONMENTAL HAZARDS:

A. Disaster hazard: highly dangerous when heated to decomposition or on contact with water or steam; it will react to produce highly toxic & corrosive fumes.

B. Occupational exposure: because of high degree of irritant properties resembling those of phosgene, it is improbable that anyone would voluntarily remain in areas with high enough concentration to exert cyanide poisoning.

C. Must be stored in well ventilated, cool, dry areas. Building must be waterproof, located on high ground.

TABLE 19. CYANOGEN CHLORIDE DETECTING REAGENTS

Reagents	Method Matrix	Interferences	Sample Type of Matrix	Sensitivity	# of Operator Steps	Ref No.
1. 1-Phenyl-3-methyl-5-pyrazolone; pyridine	silica gel	Cyanogen halides, other than chlorine	air	Not Available	1	46
2. 4-Benzylpyridine; Barbituric acid	crayon	Cl_2, phosgene, Bromobenzyl cyanide, chloropicrin	air	1 mg/m^3	1	47
3. Potassium iodide; Sodium thiosulfate	titration		liquid	Not Available	numerous	48
4. Ethyl acetoacetate; Ethyl benzoylacetate; or Diethylacetonedicarboxylate	photometric		liquid or air	Not Available	2	49
5. Sodium sulfide	alumina gel		air	Not Available	1	50
6 1,4-Diaminobenzene; Pyridine	colorimetric		liquid or gas	10^{-6} to $5x10^{-5}$M	complex	51
7. Draeger detection tube	silica gel	Cyanogen bromide	gas	.60 mg/m^3	1	35

TABLE 20. TOXICITY AND COST OF CYANOGEN CHLORIDE DETECTING REAGENTS

Reagents	Toxicity - Acute Local[3]	Cost - $ [38,39,40]
1. 1-Phenyl-3-methyl-5-pyrazolone; Pyridine	Unknown; Irritant 1, Ingestion 1; Inhalation 1	Not readily available from sources checked; 500g-12.85
2. 4-Benzylpyridine; Barbituric acid	Unknown; Irritant 2, Allergen 1, Ingestion 3, Inhalation 3	25g-4.90; 100g-6.60
3. Potassium iodide; Sodium thiosulfate	Variable; Ingestion 1	50g-39.00; 250-5.60
4. Ethyl acetoacetate; Ethylbenzoylacetate; or Diethylacetone dicarboxylate	Irritant 2; Ingestion 2; Unknown; Unknown	1kg-12.50, 100g-7.50; 50g-11.90
5. Sodium sulfide	Sulfides - Variable	500g-14.65
6. 1,4-Diaminobenzene; Pyridine	Irritant 2; Allergen 2; Irritant 1, Ingestion 2, Inhalation 1	500g-21.55; 500g-12.85
7. Draeger detection tube	None - Closed tube	1.00 to 2.00 each tube

0 NONE: (a) No harm under any conditions: (b) Harmful only under unusual conditions or overwhelming dosage.

1 SLIGHT: Causes readily reversible changes which disappear after end of exposure.

2 MODERATE: May involve both irreversible and reversible changes not severe enough to cause death or permanent injury.

3 HIGH: May cause death or permanent injury after very short term exposure to small quantities.

(1) Pyridine and 1-Phenyl-3-methyl-5-pyrazolone [46] - This procedure is a sensitive colorimetric method for the qualitative and quantitative analysis of cyanogen halides. Filter paper or silica gel is impregnated with a reagent containing pyridine and 1-phenyl-3-methyl-5-pyrazolone. If a cyanogen halide is present the reagent will undergo a change from magenta to deep blue. This test may also be modified for the detection of hydrogen cyanide. This method, although not commercially available, does appear promising. We will consider this approach in the event that commercially available techniques prove unsatisfactory.

(2) 4-Benzylpyridine and Barbituric Acid [47] - The method described below utilizes a detector crayon to determine the presence of cyanogen chloride in an air sample. Crayons are produced by mixing detector reagents with blanc fixe (precipitated barium sulfate) and then compressing the mixture to make the crayon. The ingredients for the crayon are 10 percent 4-benzylpyridine, 4 percent barbituric acid, and 86 percent neutral, dry, amorphous blanc fixe. The ingredients are thoroughly mixed, the liquid benzylpyridine is completely absorbed by the other dry components. Approximately 15 g of the mixture is then used to make a crayon.

The white marks made by the crayon first turn red and then blue in the presence of cyanogen chloride. This method of detection was found to detect 1 mg of cyanogen chloride per cubic meter with a reaction time of 1 minute. In addition, when stored at room temperature the crayons are stable for at least 3 years. However, high concentrations of chlorine, phosgene, bromobenzyl cyanide and chloropicrin interfere with this method. This procedure, like the previous method, looks promising, but is not commercially available. Therefore, it will be considered as an alternative procedure.

(3) Potassium Iodide and Sodium Thiosulfate [48] - This method involves adjusting the pH of a small test solution to 9 with either ammonium hydroxide or hydrochloric acid. Ten ml of hydrogen sulfide solution and 10ml of 0.1M ammonium hydroxide are added to the solution and boiled for 20 minutes with 0.5 g of boric acid. The solution is then cooled and brought up to a volume of 50ml. Five ml of 20 percent orthophosphoric acid and a small excess of bromine are then added, and the excess bromine is removed by adding 5ml of 5 percent hexanol. At this point, 0.5 g of potassium iodide and 5ml of 20 percent hydrochloric acid are added to the solution which is left standing for 20 minutes. The solution is then titrated with 0.01N sodium thiosulfate with starch serving as the indicator. This technique is very time consuming (minimum of one hour) and does not appear as attractive as other approaches. We do not believe that this method warrants any future consideration.

(4) Ethyl Acetoacetate, Ethyl Benzoylacetate, or Diethyl Acetonedicarboxylate [49] - Any one of these three reagents will detect the presence of cyanogen chloride. The method of detection is as follows: The sample in question is allowed to react with excess pyridine. If cyanogen chloride is present it reacts with the pyridine to form glutaconic aldehyde. This substance in solution with ethyl acetoacetate produces an orange-red color with a maximum absorption at 510 mμ. Ethyl benzoylacetate behaves similarly with a violet-ret color change occurring with a maximum absorbance of 520 mμ. Diethyl acetonedicarboxylate is the most sensitive of the three compounds, producing a reddish-violet color which has a maximum absorbance at 525 mμ. This approach does not appear as advantageous as other procedures considered. We will not consider this method as a field detection method for cyanogen chloride.

(5) Sodium Sulfide [50] - Cyanogen chloride is detected by passing a gas sample through a test tube containing alumina gel impregnated with a sodium sulfide solution. The alkali metal thiocyanate that is formed is then detected with an hydrochloric acid solution of a ferric salt which has been added to the reacting compound. This approach will be considered as an alternative method if necessary.

(6) 1,4-Diaminobenzene and Pyridine [51] - This procedure uses hydrochloric acid solutions of 1,4-diaminobenzene and pyridine to react with cyanogen chloride to yield a solution which absorbs radiation at 515nm. Oxidizing chlorine species which act as interferences can be removed by treating the sample with a mixt. of hydrochloric acid, arsenic oxide and potassium bromide. Sulfur dioxide interferences are removed by addition of barium nitrate to the colorimetric reagent. This approach will detect cyanogen chloride in the 10^{-6} to 5×10^{-5} molar range. However, we believe that the various detector tube methods listed are more advantageous so this technique will not be further considered.

(7) Draeger (CH 19601) [35] - A gas detection tube is available from Draeger for the detection of cyanogen chloride in the 0.63 to 12.55 mg/m^3 range. One to twenty strokes on the Draeger pump are required to cover this range. The only listed interference is cyanogen bromide which interferes when present at concentration levels much higher than cyanogen chloride. For example, the total indicating layer is discolored with a cyanogen bromide concentration of 108 mg/m^3 and six pump strokes. This Draeger tube is significantly less sensitive to cyanogen bromide. The relative standard deviation for the measurement of cyanogen chloride is 15 to 20 percent, depending on the actual level being measured. This colorimetric detection method appears to be the best commercially available

candidate for the analysis of cyanogen chloride. Neither Matheson or MSA listed a comparable gas detection tube for the measurement of cyanogen chloride.

DICHLORODIETHYL SULFIDE (MUSTARD GAS)

The physical and chemical properties of mustard gas are given in Table 21. Also included in this table are data pertaining to the toxicological properties of mustard gas as well as to its manufacturer. Table 22 contains a summary of information concerning each of the detection reagent systems. The toxicity and price of each reagent system are given in Table 23. Each of the detection reagent systems is discussed in detail in the following sections.

Dichlorodiethyl Sulfide (Mustard Gas) Detection Reagent Recommendations

There are no methods that are definitely commercially available for the detection of mustard gas; method 3 appears to be the most promising detection system. This method is very specific for mustard gas and the reagent is not very toxic. No precleanse reagent appears necessary. It appears that this reagent system could be incorporated into a gas detection tube.

Methods 2 and 5 also appear promising as mustard gas detection systems and will be considered as alternatives. It is possible that both these methods might also be incorporated into gas detection tubes.

TABLE 21. PROPERTIES OF DICHLORODIETHYL SULFIDE[3,4,25,26,27]

NAME OF SUBSTANCE:	Bis(2-chloroethyl)sulfide
MOLECULAR FORMULA:	$C_4H_8Cl_2S$
MOLECULAR WEIGHT:	159.08
CAS REGISTRY NUMBER:	505-60-2
WISWESSER LINE NOTATION:	G2S2G
SYNONYMS:	A. 1,1'-Thiobis(2-chloroethane) B. Bis(beta-chlorethyl)sulfide C. 1-Chloro-2-(beta-chloroethylthio)ethane D. 2,2'-Dichlorodiethyl sulfide E. Di-2-chloroethyl sulfide F. Beta, beta'-dichloroethyl sulfide G. Mustard gas H. Sulfur mustard I. Sulfur mustard gas J. Yellow cross liquid K. 2,2'-Dichloroethyl sulfide L. Bis(2-chloroethyl) sulfide M. Sulphur mustard N. Sulphur mustard gas O. Mustard vapor P. Bis(beta-chloroethyl) sulphide Q. Bis(2-chloroethyl) sulphide R. Beta, beta-dichlor-ethyl-sulphide S. 2,2'-Dichloroethyl sulphide T. Distilled mustard U. 2,2'-Dichloroediethyl sulphide V. Di-2-chloroethyl sulphide W. Beta,beta'-dichloroethyl sulphide
MELTING POINT:	13-14°C
BOILING POINT:	215-217°C @ 760 mm Hg
DENSITY/SPEC GRAVITY:	1.2741 g/l @ 20°C liquid at 4°C.

(continued)

TABLE 21 (continued)

VAPOR PRESSURE:	0.090 mm Hg @ 30°C
COLOR/FORM:	A. Colorless oily liquid B. Yellow prisms @ 13°C
SOLUBILITY:	A. Sparingly soluble in water (0.68 g/l @ 25°C) B. Soluble in fat, fat solvents, common organic solvents
STABILITY/SHELF LIFE:	A. Hydrolyzed in aqueous solution (T/2, 5 min. at 37°C); products of hydrolysis are thiodiglycol and hydrochloric acid B. Volatile with steam C. Hydrolyzed by alkalies
EXPLOSIVE LIMITS:	No information available
MAJOR USE:	A. Vesicant in chemical warfare. B. Model compound, in biological studies on alkylating agents.
SPECTRAL & OTHER PROPERTIES:	A. Flash point: 91°C B. Freezing point: 14.4°C C. Reacts with sulfhydryl & imidazole groups D. Weak, sweet, agreeable odor E. Density: 1.338 g/l @ 13°C (solid) F. Index of refraction: 1.5312 @ 20°C/D G. Vapor density: 5.4 g/l H. Mustard gas in an aqueous medium rearranges into a cyclic sulfonium form which is highly reactive. I. First order rate constant for reaction with water @ 37°C K'O (H-1)= 33/seconds J. Substrate constant S= 0.95; value of S= 1.00 for methyl bromide is the reference standard K. Shows SN1-type kinetics but may react through SN2 mechanism.

(continued)

(continued)

TABLE 21 (continued)

TOXICITY VALUES

A. LD_{50} Guinea pigs percutaneous 20 mg/kg

B. LD_{Lo} Rats percutaneous 18 mg/kg

C. LD_{50} Rats subcutaneous 3200 µg/kg

D. LC_{Lo} Mice inhalation 180 mg/m^3/10 min

E. LD_{50} Mice percutaneous 92 mg/kg

F. LD_{Lo} Mice subcutaneous 4 mg/kg

G. TD_{Lo} Mice subcutaneous 6 mg/kg/6 wk intermittent: toxic effects: carcinogenic

H. LD_{50} Mice intravenous 8600 µg/kg

I. TD_{Lo} Mice intravenous 60 µg/kg/6 days intermittent: toxic effects: carcinogenic

J. LD_{50} Dogs percutaneous 20 mg/kg

K. LD_{50} Rabbits intravenous 1100 µg/kg

L. LD_{50} Rabbits percutaneous 100 mg/kg

M. LD_{50} Rats intravenous 700 µg/kg

N. TC_{Lo} Rats inhalation 100 $\mu g/m^3$/12 wk: toxic effects: mutagenic

O. TD_{Lo} Rats inhalation 100 $\mu g/m^3$/1 yr intermittent: toxic effects: mutagenic

P. LC_{50} Rats inhalation 420 mg/m^3/2 min.

Q. TC_{Lo} Mice inhalation 1105 mg/m^3/15 min. continuous: toxic effects: carcinogenic

R. Toxic hazard rating: chronic local: irritant 3; inhalation 3; skin absorption 3. Chronic systemic: irritant 3; inhalation 3; skin absorption 3. 3=high: may cause death or permanent injury after very short exposure.

S. Toxic hazard rating: acute local: irritant 3; ingestion 3; inhalation 3. Acute systemic: ingestion 3; inhalation 3; skin absorption 3. 3=high: may cause death or permanent injury after very short exposure to small quantities.

(continued)

TABLE 21 (continued)

T. LC_{Lo} Human inhalation 149.50 mg/m^3/10 min; LD_{Lo} human percutaneous 64 mg/kg; LC_{50} human inhalation 1500 mg/m^3/min.

U. Representative oncogenesis tests in strain mice via IV injection of 0.25 ml of saturated aqueous solution mustard gas for 112 days induced 93% lung adenomas, 61% in controls.

V. 16 C3H mice of both sexes, 10 female C3HF mice & 30 A mice were given 5-6 weekly SC injections of 0.05% soln of mustard gas. Fibrosarcomas at injection site were observed in 1/8 C3H males, 2/9 C3HF females & 1/14 A males 10-14 mos. after beginning of treatment.

W. 16 C3H mice 10 female C3HF mice & 30 A mice were given 5-6 weekly SC injections of 0.05 ml of 0.05% soln of mustard gas. In a second experiment a rhabdomyosarcoma occurred after 15 mos. in 1/24 C3H males, & local sarcomas were observed in 2/38 C3HF males about 15 mos. after start of treatment.

X. A group of 40 male & 40 female A mice, 2-3 months of age, was exposed for 15 min to vapors from 100 cm^3 mustard gas in an 8-L dessicator 4 months after exposure 30 test & 32 control mice were killed, & incidences of lung tumors were found to be 9/30 & 6/32 respectively.

Y. 15 male & 15 female A mice 2 mos. old were injected IV on alternate days with 0.25 ml of 1:10 dilution of saturated solution of mustard gas in water (0.06-.07%) for 4 injections. Survivors were killed at age of 6 mos., & 14/15 had developed pulmonary tumors compared with 15/28 controls.

Z. Dominant lethal mutations in adult male virgin rats were induced after exposure to mustard gas @ 0.1 mg/m^3 of air for 52 wks.

AA. Mustard gas induce(s) mutations & chromosome rearrangements in Drosophila melanogaster & mutations in specific DNA regions. It induces chromosome aberrations in cultured rat lymphosarcoma cell lines.

(continued)

TABLE 21 (continued)

BB. Pharmacodynamic action: At low concentration, it has been shown to inhibit DNA synthesis in E. Coli bacteria, in Hela cells, in L-Cells, & Chinese hamster cells.

CC. (35)S-labelled mustard gas injected IP in mice produced alkylation of nucleic acids in ascite tumor tissue.

THRESHOLD LIMIT VALUE: No information available

PHYSIOLOGICAL EFFECTS:

A. Carcinogenic determination: human suspected.

B. May possibly cause genetic mutations in man.

C. Produces delayed effects and mortality.

MANUFACTURING INFO.:

A. Prepared by treating ethylene with sulfur chloride (Levinstein Process).

B. By treating beta'-dihydroxyethyl sulfide with HCl gas (German Process).

PRODUCTION: No information available

MANUFACTURERS: No information available

ENVIRONMENTAL HAZARDS:

A. Disaster hazard: dangerous; highly volatile toxic gas when heated to decomposition or on contact with acid or acid fumes, it emits highly toxic fumes of oxides of sulfur & chlorides; it will react with water or steam to produce toxic & corrosive fumes; it can react vigorously with oxidizing materials.

B. Fire hazard: slight, when exposed to heat or flame; can be ignited by a large explosive charge.

C. Firefighting methods: water, foam, carbon dioxide, dry chemical.

TABLE 22. DICHLORODIETHYL SULFIDE (MUSTARD GAS) DETECTING REAGENTS

Reagents	Method Matrix	Interferences	Sample Type Matrix	Sensitivity	# of Operator Steps	Ref No.
1. Methyl red	Paper	Arsine, Acid gases	air	Not Available	1	52
2. Sodium iodoplatinate	Paper		air	Not Available	2	31
3. Gold chloride	Granulated Adsorbent		air	Not Available	2	53
4. Iodine trichloride; Sodium N-chloro-p-toluenesulfonamide	Colorimetric		air	5.0 mg/m^3	3	54
5. Starch; Hydriodic acid	Silica gel		air	Not Available	2	55
6. Dragendoff reagent	Water		60% EtOH	Sample Size Not Given	4	56
7. Dichloramine T	Titration		Organic Solvents	Not Available	2	57
8. Soda, Carbon; Caustic soda; Silver coin; Sodium nitroprusside	Carbon rod Colorimetric soln		solid	1940 mg/m^3	11	43
9. DB-3 Gel; Ethanol; Potassium hydroxide	Gel		air	Not Available	3	58
10. Iodoplatinate; Potato starch	Paper	Chlorine, nitrous fumes, reducing agents	liquid or gas	10.0 mg/m^3	4	59

TABLE 23. TOXICITY AND COST OF DICHLORODIETHYL SULFIDE (MUSTARD GAS) DETECTING REAGENTS

Reagents	Toxicity - Acute Local[3]	Cost - $[38,39,40]
1. Methyl red	Ingestion 1, Carcinogen determination indefinite	10g-5.70
2. Sodium iodoplatinate	No information available on specific compound, however, platinum salts-Inhalation 2, Iodides-Variable	1g-19.50
3. Gold chloride	Gold Compounds-Allergen 2, Chloride-Variable	1g-23.00
4. Iodine trichloride; Sodium N-chloro-p-toluenesulfonamide	Ingestion 3, Inhalation 3, Irritant 3; Unknown	100g-16.00; 100g-21.00;
5. Starch; Hydriodic acid	Allergen 1; Inhalation 1; Irritant 3; Ingestion 3, Inhalation 3	1kg-14.50; 200g-12.00
6. Dragendoff reagent	No information available	2.00
7. Dichloramine T	Irritant 1	20g-14.50
8. Soda; Carbon; Caustic soda; Silver coin; Sodium nitroprusside	Irritant 2, Ingestion 2, Inhalation 2; Inhalation 2, Ingestion 3, Inhalation 2, Irritant 3, Inhalation 2, Ingestion 3	2kg-10.50; 500g-7.85; 2kg-12.00 100g-8.50
9. DP-3 Gel; Ethanol; Potassium hydroxide	No information available; Irritant 1, Inhalation 1; Ingestion 3, Irritant 3	10g-17.00; 4kg-9.00; 2kg-14.00

0 NONE: (a) No harm under any conditions: (b) Harmful only under unusual conditions or overwhelming dosage.

1 SLIGHT: Causes readily reversible changes which disappear after end of exposure.

2 MODERATE: May involve both irreversible and reversible changes not severe enough to cause death or permanent injury.

3 HIGH: May cause death or permanent injury after very short term exposure to small quantities.

U Unknown-No valid information available on Humans

(continued)

TABLE 23 (continued)

Reagents	Toxicity - Acute Local[3]	Cost - $[38,39,40]
10. Iodoplatinate; Potato starch	No information on specific compound, however, Platinum Salts-Inhalation 2, Iodides-Variable; Allergen, Inhalation 1	1g-19.50; 2kg-14.00

0 NONE: (a) No harm under any conditions: (b) Harmful only under unusual conditions or overwhelming dosage.

1 SLIGHT: Causes readily reversible changes which disappear after end of exposure.

2 MODERATE: May involve both irreversible and reversible changes not severe enough to cause death or permanent injury.

3 HIGH: May cause death or permanent injury after very short term exposure to small quantities.

U Unknown-No valid information available on Humans

(1) Methyl Red [52]- Filter paper impregnated with a solution containing 0.05 g methyl red dissolved in 100 ml alcohol at 60°C will turn pink in the presence of mustard gas. Arsines give the same reaction due to the acid produced when they are hydrolyzed. Acid gases will give a positive test. This method is not considered a promising candidate since it is likely to encounter many interferences. Also methyl red is considered to be a possible carcinogen.

(2) Sodium Iodoplatinate [31] - Filter paper is moistened with a 2 percent solution of sodium iodoplatinate; the paper will then detect mustard gas by turning first a purple-red and then blue. No additional information was available pertaining to sensitivity or interference levels.

This method is not commercially available but seems worthy of consideration as an alternate approach.

(3) Gold Chloride [53]- This technique is similar to the second method mentioned above. A gas detector tube is prepared by filling a small cylinder with a colorless granulated adsorbent impregnated with gold chloride. The sample is drawn through the adsorbent and a reddish-brown color change denotes the presence of mustard gas. Allyl mustard oil, diphenylaminochloroarsine, ethyldichloroarsine, and thiodiglycol desensitize the reaction somewhat. The method is not influenced by the presence of other Class A poisons such as hydrogen cyanide, lewisite or phosgene. Because of the reddish-brown color change, this method appears to be fairly specific for mustard gas.

(4) Iodine Trichloride and Sodium N-Chloro-p-toluenesulfonamide [54] This method involves mixing the suspect sample first with iodine trichloride and then treating the resulting mixt. with a 4 percent aqueous solution of sodium N-chloro-p-toluenesulfonamide. A brownish-red color that is stable for several hours indicates the presence of mustard gas. This test is sensitive down to 5mg of mustard gas per cubic meter. The reagents used in this detection system are highly toxic. Little information was available pertaining to interferences or stability of the reagents. This method does not look to be very promising due to the toxicity of the reagents, but will not be totally ruled out as a candidate.

(5) Starch and Hydriodic Acid [55]- This method involves passing test air through a tube containing silica gel and soluble starch. The mixt. is then treated with hydriodic acid which will turn blue in the presence of mustard gas. Little information was available on this detection system as far as sensitivity and interference levels. This approach will not be ruled out at this point.

(6) Dragendoff Reagent [56]- The reagent consists of (a) 8 g of basic bismuth nitrate dissolved in 20ml of 30 percent nitric acid and (b) 27 g of potassium iodide dissolved in a small volume of water. Three ml of this reagent is then mixed with 3ml of a 60 percent ethanol solution containing mustard gas. A red-brown precipitate is formed with concentrated solutions of mustard gas whereas the solution becomes turbid with dilute solutions. This method is capable of detecting 0.13 g of mustard gas per liter of the ethanolic solution.

This method is not commercially available and does not seem very promising. One of the biggest disadvantages of this method is that it is not very sensitive. It does not seem necessary to examine this method further.

(7) Dichloramine T [57]- This technique involves the quantitative catalyzing action of sulfide on the reduction of dichloramine T in the presence of cyclohexanol. Mustard gas can be determined by the iodmetric titration of the residual chlorine from dichloramine T reacting with mustard in organic solvents. The end point of the titration is sufficiently sharp so that the addition of starch is not necessary.

This method utilizes a titration technique which would require an experienced technician plus extensive equipment and time. This method does not seem to be very promising and will therefore not be considered further.

(8) Soda, Carbon Caustic Soda, Silver Coin, Sodium Nitroprusside [43] This method is for the determination of sulfur. A sample of substance possibly containing sulfur is collected onto a carbon rod. To this is added water, soda, heat, and a caustic soda solution. The rod is then heated in a reducing flame and, if sulfur is present, sodium sulfide will be formed. This is determined by touching the rod to a silver coin and, if sodium sulfide is present, a brown stain develops. Also a few drops of sodium nitroprusside will give a violet color in the presence of sulfide.

This method seems unsuitable for the field screening for mustard gas. The method is specific for sulfur, and any substance that contains sulfur will give a positive result. It is also a time consuming process. This method will not be considered for laboratory evaluation.

(9) DB-3 Gel, Ethyl Alcohol, Potassium Hydroxide [58]- In this method, a few granules of DB-3 silica gel are added to a portion of silica gel and ethyl-alcohol added. The mixt. is then ignited and 20 percent potassium hydroxide added to make it alkaline. If mustard is present in the air, some of the granules will turn blue.

This method is not commercially available and does not seem very promising. This method will not be examined further.

(10) Iodoplatinate, Potato Starch, Acetic Acid [59]- This method involves passing an air sample through 1.0ml of 5 percent acetic acid solution. Mustard gas in the sample is absorbed into the acetic acid. Iodoplatinate and potato starch are added to this sample and, if mustard gas is present, a blue color develops. Mustard gas absorbed by the acetic acid can be determined with an accuracy of 1 μg by comparing the intensity of the blue color with a series of standards.

This method does not seem suitable for screening mustard gas. The main reason for this is the need for standards to do the determination. Also it is not positive that this method is adaptable to a detector tube.

DIPHOSGENE

The physical and chemical properties of diphosgene are given in Table 24. Also included in this table are data pertaining to the toxicological properties of diphosgene. Table 25 contains a summary of information concerning possible detection systems. Each of these detection systems is discussed in the following sections.

Diphosgene Detection Reagent Recommendations

The literature search for diphosgene was not very successful. We were able to find very little information pertaining to diphosgene specifically. However, we did discover that diphosgene completely decomp. to phosgene when heated to 300 - 350°C. Using this as a basis, we will attempt to use the phosgene methods for detecting diphosgene.

Two types of experiments will be conducted, one using a preheating chamber and one not using the preheating chamber. Both sets of experiments will be coupled with the more promising detection methods. Should the heated tube method be the most promising approach, various halocarbons will have to be evaluated as potential interferences.

TABLE 24. PROPERTIES OF DIPHOSGENE[3,4,25,26,27]

NAME OF SUBSTANCE:	Diphosgene
MOLECULAR FORMULA:	$C_2Cl_4O_2$
MOLECULAR WEIGHT:	197.83
CAS REGISTRY NUMBER:	503-38-8
WISWESSER LINE NOTATION:	GVOXGGG
SYNONYMS:	A. Perchloromethyl formate B. Superpalite C. Trichloromethyl chloroformate D. Methanol, Trichloro-, Chloroformate E. Formic acid, Chloro-, trichloromethyl ester F. Carbonochloridic acid, trichloromethyl ester G. Diphosgene
MELTING POINT:	-57°C
BOILING POINT:	128°C
DENSITY/SPEC GRAVITY:	1.6525 g/l @ 14°C
VAPOR PRESSURE:	10 mm Hg @ 20°C
COLOR/FORM:	Colorless liquid
SOLUBILITY:	Insoluble in water, soluble in ethanol, very soluble in ether.
STABILITY/SHELF LIFE:	No information available
EXPLOSIVE LIMITS:	No information available
MAJOR USES:	Military poison
SPECTRAL & OTHER PROPERTIES:	A. Index of refraction: 1.4566 @ 22°C/D B. Vapor density: 6.9 g/l C. Odor of new-mown hay D. Decomp. completely at 300 to 350°C to phosgene.

(continued)

TABLE 24 (continued)

TOXICITY VALUES:	A. LD_{LO} Mice inhalation 344 mg/m^3
	B. Toxic hazard rating: acute local: irritant 3; ingestion 3; inhalation 3. Acute systemic: ingestion 3; inhalation 3; 3-high: may cause death or permanent injury after very short exposure to small quantities.
THRESHOLD LIMIT VALUE:	Phosgene - 0.413 mg/m^3
PHYSIOLOGICAL EFFECTS:	A. It is a lung irritant. It is slightly lacrimatory. Its physiological action, like phosgene, is delayed.
	B. Eye irritation, irritation of upper respiratory tract, & surface burns have been principal findings in exposed humans. Pulmonary edema would undoubtedly occur with higher levels of exposure. Eye irritation may persist some time after exposure ceases. Skin sensitization may occur. (Chloroformates)
MANUFACTURING INFO:	No information available
PRODUCTION:	No information available
MANUFACTURERS:	No information available
ENVIRONMENTAL HAZARDS:	A. Occupational exposure: no effects on general health nor in laboratory findings (blood studies & liver function tests) of persons manufacturing chloroformates were noted. (Chloroformates)
	B. Dangerous when heated, it emits highly toxic fumes; will react with water or steam to produce toxic and corrosive fumes.
	C. These materials should be handled so as to prevent all contact & with due regard for their corrosive & flammable nature. Air-supplied respirators & facilities for flushing eyes & skin with water should be provided. (Chloroformates)
	D. Special attention should be given eyes & respiratory tract in medical examinations. (Chloroformates)
	E. To decontaminate in enclosed spaces, use amonia or steam.
	F. It is moderately persistent.

TABLE 25. DIPHOSGENE DETECTING REAGENTS

Method	Reason[42]	Reference
1. Use of a preheating chamber plus methods of phosgene	Diphosgene completely decomp. to phosgene at 300 to 350°C	For further information on phosgene methods, see the section on phosgene
2. Other - Methods of detecting diphosgene without preheat treatment	Methods that detect phosgene may also detect diphosgene without preheating chamber	For further information on phosgene methods, see the section on phosgene

(1) Phosgene Methods With Preheating Chamber [42]- The basis for this method is that diphosgene decomposes completely to phosgene when heated to 300-350°C. It is envisioned that the methods for detecting phosgene will then be used to detect the decomposed phosgene. There may be an interference problem associated with the pyrolysis, this will have to be determined in the laboratory.

For discussions on phosgene methods, consult that section pertaining to detection of this substance.

(2) Other - It may be possible that diphosgene will react similarly to phosgene. On the basis of this supposition, we will use the phosgene methods without the preheating chamber to see if this assumption is valid.

ETHYLDICHLOROARSINE - METHYLDICHLOROARSINE

The physical and chemical properties of ethyl and methyldichloroarsine are given in Tables 26 & 27. Also given in the tables are the toxicological properties of ethyl and methyldichloroarsine as well as to their manufacturer. Table 28 contains a summary of information concerning each of their detection reagent systems. The toxicity and price of each reagent system are given in Table 29. Each of the detection reagent systems is discussed in detail in the following sections.

Ethyl and Methyldichloroarsine Detection Reagent Recommendations

Method 16 appears to be the most promising method found for ethyl and methyldichloroarsine. This method is supposedly highly sensitive and specific as an indicator for alkyldichloroarsines and closely related organoarsenic halides. The reagent system is impregnated into silica gel and used as an indicator for the above gases. Method 1 will be selected as the primary alternative since it also looks as if it could be incorporated into a gas detector tube.

TABLE 26. PROPERTIES OF ETHYLDICHLOROARSINE[3,4,25,26,27]

NAME OF SUBSTANCE:	Ethyldichloroarsine
MOLECULAR FORMULA:	$C_2H_5ASCl_2$
MOLECULAR WEIGHT	174.89
CAS REGISTRY NUMBER:	598-14-1
WISWESSER LINE NOTATION:	G-As-GZ
SYNONYMS:	A. Dick (German) B. Ed C. TL 214 D. Arsonous dichloride, ethyl E. Arsenic, dichloroethane F. Dichloroethylarsine G. Arsine, dichloroethyl
MELTING POINT:	-65°C
BOILING POINT:	156°C (Decomp.)
DENSITY/SPEC GRAVITY:	1.742 g/l at 14°C
VAPOR PRESSURE:	2.29 mm Hg at 21.5°C
COLOR/FORM:	A. Colorless B. Mobile liquid
SOLUBILITY:	A. Slightly soluble in water B. Soluble in all proportions of alcohol C. Soluble in all proportions of ether
STABILITY/SHELF LIFE:	Volatility: 20,000 mg/m^3 at 20°C
EXPLOSIVE LIMITS:	No information available
MAJOR USES:	Military poison
SPECTRAL AND OTHER PROPERTIES:	A. Biting, irritant odor B. Fruit-like odor (High Dilution) C. Decomp. by water D. Attacks brass, but not iron (dry).

(continued)

TABLE 26. (continued)

E. Coefficient of thermal expansion 0.0011

F. Vapor density - 6 g/l (air=1)

G. Becomes yellowish under the action of light and air.

TOXICITY VALUES:

A. LC_{Lo} Mice inhalation 160 mg/m^3/10 min.

B. LC_{Lo} Mice inhalation 673 mg/m^3/20 min.

C. LC_{Lo} Cats inhalation 85.92 mg/m^3/40 min.

D. LD_{Lo} Cats subcutaneous 1 mg/kg

E. Aquatic toxicity TLm: under 7.16 mg/m^3/96 hrs.

F. Acute = very high via inhalation & probably high via oral routes as well. Very irritating. High = capable of causing death or permanent injury due to exposures of normal use, incapacitating & poisonous; requires special handling.

THRESHOLD LIMIT VALUE: No information available

PHYSIOLOGICAL EFFECTS: Is an extremely poisonous liquid with vapor that is extremely powerful lacrimatory irritant of eyes & nose, also very irritating to skin & respiratory tract. The vapor is said to cause necrosis of corneal epithelium.

MANUFACTURING INFO: Derived by chlorination of ethyl arsinous oxide.

PRODUCTION: No information available

MANUFACTURERS: No information available

ENVIRONMENTAL HAZARDS: Dangerous on contact with acid or acid fumes, emits highly toxic fumes of arsenic & phosgene will react with water or steam to produce toxic & corrosive fumes. Can react with oxidizing materials.

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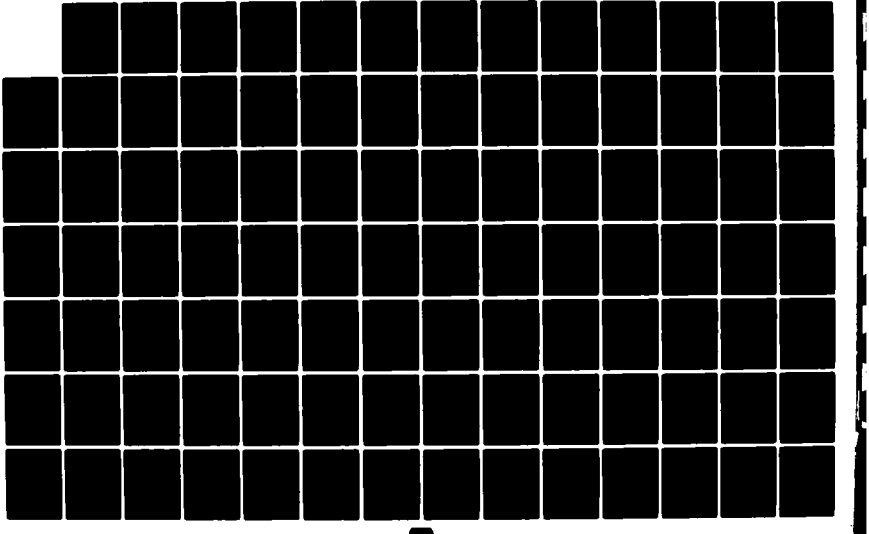

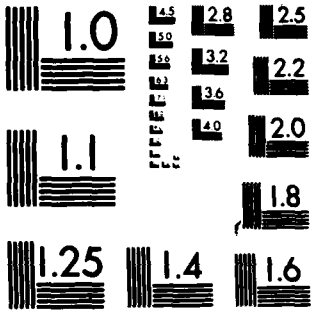

MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

TABLE 27. PROPERTIES OF METHYLDICHLOROARSINE[3,4,25,26,27]

NAME OF SUBSTANCE:	Methyldichloroarsine
MOLECULAR FORMULA:	CH_3AsCl_2
MOLECULAR WEIGHT	160.86
CAS REGISTRY NUMBER:	593-89-5
WISWESSER LINE NOTATION:	G-As-Gl
SYNONYMS:	A. Arsenous dichloride, methyl- B. Dichloromethylarsine C. Methylarsine dichloride D. Arsine, dichloromethyl
MELTING POINT:	-59.0°C
BOILING POINT:	136.0°C
DENSITY/SPECIFIC GRAVITY:	1.838 g/l at 20°C/4°C
VAPOR PRESSURE:	8.5 mm Hg at 20°C
COLOR/FORM:	A. Colorless B. Mobile liquid
SOLUBILITY:	A. Slightly soluble in water B. Very soluble in alcohol C. Soluble in ether
STABILITY/SHELF LIFE:	No information available
EXPLOSIVE LIMITS:	No information available
MAJOR USES:	Military poison
SPECTRAL AND OTHER PROPERTIES:	No information available
TOXICITY VALUES:	A. Inhalation mouse: LC_{Lo} 270 mg/m^3/10 min. B. Toxicity hazard rating: acute local: irritant 3; ingestion 3; inhalation 3. 3=high: may cause death or permanent injury after very short exposure to small quantities.

(continued)

TABLE 27 (continued)

THRESHOLD LIMIT VALUE:	No information available
PHYSIOLOGICAL EFFECTS:	A. Acute poisoning. Ingestion of arsenic compounds results in marked irritation of the stomach and intestines, with nausea, vomiting and diarrhea. B. In severe cases the vomitus and stool are bloody and the patient goes into collapse and shock with weak, rapid pulse, cold sweats, coma and death. C. Chronic arsenic poisoning: disturbance in digestive system; liver damage; disturbance of blood, kidneys and nervous system; skin abnormalities.
MANUFACTURING INFO:	No information available
PRODUCTION:	No information available
MANUFACTURERS:	No information available
ENVIRONMENTAL HAZARDS:	A. When heated to decomposition it emits highly toxic fumes of arsenic and chlorine. B. Will react with water, steam, or acids to produce toxic and corrosive fumes.

TABLE 28. ETHYLDICHLOROARSINE - METHYLDICHLOROARSINE DETECTING REAGENTS

Reagents	Method Matrix	Interferences	Sample Type Matrix	Sensitivity	Operator Steps	Ref No.
1. Michler's thioketone	Crayon	Lewisite, Phosgene	gas	Not Available	1	47
2. Mercurous nitrate	Precip.		liquid or gas	Not Available	1	42
3. 2,4-Dinitro-6-chlorophenol	Paper		gas or liquid	Not Available	2	53
4. Trinitrocresol	Paper		liquid or gas	Not Available	2	60
5. 2,4-Dinitrodiethylaniline	Paper		liquid or gas	Not Available	2	60
6. 8-Nitroquinoline	Paper		liquid or gas	Not Available	2	60
7. 5-(or 8)-Nitroisoquinoline	Paper		liquid or gas	Not Available	2	60
8. 1,8-Dinitronaphthalene	Paper		liquid or gas	Not Available	2	60
9. 6-Chloro-2-cyano-3-nitrotoluene	Paper		liquid or gas	Not Available	2	60
10. p,p'-Dinitrostilbene-o,o'-disodium sulfonate	Paper		liquid or gas	30 µg	2	60
11. Ammonium molybdate	Liquid		gas or liquid	Not Available	3	61
12. Potassium iodate	Liquid		gas or liquid	Not Available	3	61
13. Selenium oxide	Liquid		gas or liquid	Not Available	3	61
14. Osmium tetroxide	Liquid		gas or liquid	Not Available	3	61
15. Hydrogen sulfide; Hydroquinone	Precip.		gas or liquid	Not Available	3	61
16. Zinc sulfate; Molybdate acid	Silica gel	Alkyl *arsines*	gas	2.5 µg	1	53

TABLE 29. TOXICITY AND COST OF ETHYLDICHLOROARSINE - METHYLDICHLOROARSINE DETECTING REAGENTS

Reagents	Toxicity - Acute Local[3]	Cost - $[38,39,40]
1. Michler's thioketone (4,4'-bis(dimethylamino) thiobenzophenone)	Ingestion 1	10g-22.00
2. Mercurous nitrate	Irritant 3; Ingestion 3, Inhalation 2	100g-16.50
3. 2,4-Dinitro-6-chlorophenol	Unknown	100g-21.00
4. Trinitrocresol	Ingestion 3, Inhalation 3	Not readily available from sources checked
5. 2,4-Dinitrodiethylaniline	Unknown	10g-26.00
6. 8-Nitroquinoline	Ingestion 3	25g-11.25
7. 5-(or 8)-Nitroisoquinoline	Unknown	10g-27.10
8. 1,8-Dinitronaphthalene	Nitro Compounds of Aromatic Compounds Irritant 1	5g-11.55
9. 6-Chloro-2 cyano-3 nitrotoluene	Unknown	Not readily available from sources checked
10. p,p'-Dinitrostilbene - O,O' disodium sulfonate	Unknown	Acid - 100g-10.50
11. Ammonium molybdate	Irritant 2, Ingestion 2, Inhalation 2	20g-47.00
12. Potassium iodate	Variable	50g-39.00

0 NONE: (a) No harm under any conditions: (b) Harmful only under unusual conditions or overwhelming dosage.

1 SLIGHT: Causes readily reversible changes which disappear after end of exposure.

2 MODERATE: May involve both irreversible and reversible changes not severe enough to cause death or permanent injury.

3 HIGH: May cause death or permanent injury after very short term exposure to small quantities.

U Unknown-No valid information available on Humans

(continued)

TABLE 29 (continued)

Reagents	Toxicity - Acute Local[3]	Cost - $[38,39,40]
13. Selenium oxide	Details Unknown, Absorption 3	25g-21.25
14. Osmium tetroxide	Irritant 2, Inhalation 3	1g-21.00
15. Hydrogen sulfide; Hydroquinone	Irritant 3, Inhalation 3; Irritant 2, Allergen 1	1 cartridge 28.50 - 20g-42.00
16. Zinc sulfate; Molybdic acid	Variable; Irritant 1	50g-34.50; 500g-14.00

0 NONE: (a) No harm under any conditions: (b) Harmful only under unusual conditions or overwhelming dosage.

1 SLIGHT: Causes readily reversible changes which disappear after end of exposure.

2 MODERATE: May involve both irreversible and reversible changes not severe enough to cause death or permanent injury.

3 HIGH: May cause death or permanent injury after very short term exposure to small quantities.

U Unknown-No valid information available on Humans

(1) 4,4'-Bis(dimethylamino)-thiobenzophenone [47]- This procedure uses a detector crayon containing 5 percent 4,4'-bis (dimethylamino)-thiobenzene (Michler's thioketone) and 95 percent blanc fixe. The light tan marks made by the crayon turn an intense green-blue on contact with either ethyldichloroarsine, its vapor, or lewisite. If the crayon mark turns purple it indicates a high concentration of phosgene. In addition, chlorine and cyanogen bromide vapors cause the marks to become grayish in color.

This method appears to be quite promising and will be reserved as an alternative to Method 16. The reasons it is considered only as an alternative to Method 16 are that the reagent is more expensive and because of the interferences.

(2) Mercurous Nitrate [42]- Ethyldichloroarsine can also be detected by aspirating a sample into a 1 ml solution of acidified (nitric acid) mercurous nitrate. A white precipitate, which changes slowly to gray, is formed if the compound is present.

This method is not commercially available as a colorimetric detection method. It also utilizes mercurous nitrate which is very toxic. It will not be examined any further.

(3) 2,4-Dinitro-6-chlorophenol [53]- This test involves treating filter paper with 20 mg/ml 2,4-dinitro-6-chlorophenol in acetone solution. The paper is then wetted by the sample in question. A few drops of 5N sodium hydroxide is then added to the paper. A color change from yellow to bright red indicates the presence of ethyl or methyldichloroarsine.

The method depends on an acid-base reaction. In this type of reaction, acid gas vapors would be interferences. Since these would be too numerous to screen out, this method does not seem suitable for this project.

(4) Trinitrocresol [60]- A saturated 95 percent ethanol/trinitrocresol solution is used to treat filter paper for this approach. The paper is then wetted by the sample in question and a few drops of 2.5N sodium hydroxide are added. A color change from yellow to bright red is an indication of ethyl or methyldichloroarsine.

For the same reason as for Method 3, this method will not be examined any further.

(5) 2,4-Dinitrodiethylaniline [60] - This technique is very similar to the above approach with the exception of using 2,4-dinitrodiethylaniline as the detecting reagent. The color changes from yellow to bright red when brought into contact with either ethyl or methyldichloroarsine.

For the same reason given under Method 3, this method will not be examined further.

(6) 8-Nitroquinoline [60]- This approach uses a saturated 95 percent ethanol solution of 8-nitroquinoline as the detecting reagent. A filter paper is treated with this solution and then a few drops of sample are added. Sodium hydroxide (5N) is used as the developing solution, which is added to the paper dropwise. A color change from pale yellow to dark purple represents a positive test.

For the same reason given under Method 3, this method will not be examined further.

(7) 5-(or 8)-Nitroisoquinoline [60]- This procedure utilizes a 95 percent ethanolic solution containing 10 mg/ml of 5-(or 8)-nitroisoquinoline as the detecting reagent. A piece of filter paper is wetted by the solution and dried. The sample in question is then brought into contact with the treated filter paper. A few drops of 5N sodium hydroxide are then added. If ethyl or methyldichloroarsine is present the paper will change from a pale yellow color to a dark purple.

For the same reason given under Method 3, this method will not be examined further.

(8) 1,8-Dinitronaphthalene [60]- Filter paper is impregnated with a 20 mg/ml solution of 1,8-dinitronaphthalene in acetone. The original color of the filter paper after treatment will be white. This is exposed to the sample and, after addition of a few drops of 10N sodium hydroxide, a color change to dark green indicates the presence of ethyl or methyldichloroarsine.

For the same reason given under Method 3, this method will not be examined further.

(9) 6-Chloro-2-cyano-3-nitrotoluene [60]- This procedure uses a saturated 95 percent ethanolic solution as the detecting reagent. Filter paper treated with this solution will change from a white appearance to a dark purple after exposure to ethyl or methyldichloroarsine and the addition of a few drops of developing solution (2.5N sodium hydroxide in 48 percent ethanol).

This method will not be examined futher for the reasons outlined in Method 3.

(10) p,p'-Dinitrostilbene-o,o'-disodium Sulfonate [60]- Filter paper is treated with a saturated 95 percent ethanol solution of this reagent. In the presence of ethyl or methyldichloroarsine,the paper will change, after a few drops of 5N sodium hydroxide, from a pale yellow to a purple red.

This method will not be examined any further for the reasons outlined in Method 3.

(11) Ammonium Molybdate [61]- This compound may be used as an indicator for arsenic-containing gas or liquid. It is based upon the oxidation - reduction reaction that occurs in the presence of ethyl or methyldichloroarsine. Ammonium molybdate is reduced to molybdenum blue by these two Class A poisons. No information was available pertaining to interferences or sensitivity levels. This method will be considered further if Method 1 or Method 16 is found to be unsatisfactory.

(12) Potassium Iodate [61]- This reagent also utilizes an oxidation - reduction reaction as its detecting principle. In the presence of ethyl or methyldichloroarsine, potassium iodate is reduced to metallic iodine, which is determined with the help of starch as an indicator. No information was available. pertaining to interferences or sensitivity levels. This method may be considered if Methods 1 and 16 prove unsatisfactory.

(13) Selenium Oxide [61]- This reagent is reduced to metallic selenium when brought into contact with either ethyl or methyldichloroarsine. An orange coloration is produced by this reduction. No information was available pertaining to sensitivity or interference levels. It may be considered if Methods 1 and 16 prove unsatisfactory.

(14) Osmium Tetroxide [61]- Like the before mentioned reagent systems, osmium tetroxide can also be used to detect ethyl or methyldichloroarsine. In the presence of either of these gases, osmium tetroxide is reduced to osmium dioxide which is black in coloration. No additional information was available. It may be considered if Methods 1 and 16 are found unsatisfactory.

(15) Hydrogen Sulfide, Hydroquinone [61]- The complex compound of hydrogen sulfide with hydroquinone is more convenient than hydrogen sulfide to use in the method. Upon action of the reagent a precipitation of arsenosulfide is formed, not only of primary, but also of secondary arsines. Since a precipitation step is involved, this reagent system will not be considered further.

(16) Zinc Sulfate and Molybdic Acid [53]- The detection of methyldichloroarsine is accomplished by preparing a 10 percent molybdate solution. This solution is prepared by making a 1 percent solution of 85 percent Molybdenum trioxide in water and then evaporating 90 percent of the water. The zinc sulfate solution is prepared by dissolving 10 g of zinc sulfate heptahydrate in 10ml of water. Ten g of silica gel are then

impregnated with 5ml of each solution. The silica gel is then capable of indicating alkyldichloroarsines and closely related organic arsenic halides.

This method appears to be the most promising; although it is not commercially available as a detector tube, it may possibly be adapted to one. Its reagents are also not very toxic.

GERMANE

Information pertaining to the detection of germane, specifically, could not be found. The detection methods identified were for germanium in general rather than for its hydride. The limited information we were able to find concerning germane is given in Table 30. The detecting reagent systems which were identified are summarized in Tables 31 and 32. A short description of each of these reagent systems is given in the following section.

Germane Detection Reagent Recommendations

Methods one and two appear to be the most promising detection reagent systems for germane. Both methods will have to be evaluated in the laboratory to determine if the hydride form of germanium can be detected by these methods. It may be necessary to precipitate the germane as germanium (x) and then perform the above analysis. This approach will require significant laboratory development effort.

TABLE 30. PROPERTIES OF GERMANE [3,4,25,26,27]

NAME OF SUBSTANCE:	Germane
MOLECULAR FORMULA:	GeH_4
MOLECULAR WEIGHT	76.63
CAS REGISTRY NUMBER:	7782-65-2
WISWESSER LINE NOTATION:	No information available
SYNONYMS:	A. Germanium tetrahydride B. Monogermane
MELTING POINT:	-165.0°C
BOILING POINT:	-90.0°C
DENSITY/SPEC GRAVITY:	3.43 g/l, liquid 1.532 at -142°C
VAPOR PRESSURE:	760 mm Hg at -88.9°C
COLOR/FORM:	Colorless gas
SOLUBILITY:	A. Slightly soluble in hot HCl B. Decomp. in HNO_3 C. Soluble in NaCCl
STABILITY/SHELF LIFE:	Thermally less stable than silanes; reacts with oxygen at 160-183°C
EXPLOSIVE LIMITS:	No information available
MAJOR USES:	*No information available*
SPECTRAL AND OTHER PROPERTIES:	Decomp. at 280°C, heat of formation 21.6 ± 0.5 Kcal/mol
TOXICITY VALUES:	Exposure limit 0.63 mg/m^3/8hr for humans.
THRESHOLD LIMIT VALUE:	Air: 0.63 mg/m^3
PHYSIOLOGICAL EFFECTS:	A. May cause hemolysis B. Local irritation
MANUFACTURING INFO:	A. Prepared by the action of lithium aluminum hydride on a germanium halide in ether solution.

(continued)

TABLE 30 (continued)

B. Prepared commonly by the reaction of a germanide, such as Mg_2Ge, with hydrochloric acid; also prepared by reduction of germanium tetrachloride with zinc and sulfuric acid.

C. Produced by reduction of GeO_2 by sodium hydroborate

PRODUCTION: No information available

MANUFACTURERS: No information available

ENVIRONMENTAL HAZARDS:

A. The volatile hydrides are flammable, some spontaneously so in air. All hydrides react violently on contact with powerful oxidizing agents. When heated or in contact with moisture or acids, an exothermic reaction evolving hydrogen occurs. Often enough heat is evolved to cause ignition.

B. Liberate hydrogen when heated or reacted with acid.

TABLE 31. GERMANE DETECTING REAGENTS

Reagents	Method Matrix	Interferences	Sample Type Matrix	Sensitivity	# of Operator Steps	Ref No.
1. Phenyl fluorone	Paper		Soln	Not Available	2	62
2. Hydroxyphenylfluorone	Paper	Molybdenum, Ceric, Permanganate, and Chromate ions	Soln	Not Available	5	62
3. Phthalic acid; Alpha napthol; Boric acid in Sulfuric acid	Colorimetric		air	Not Available	3	63
4. Hydrochloric acid; Sodium carbonate; Potassium iodate; Potassium iodide; Carbon dioxide; Starch	Titration		liquid or gas	Not Available	9	64
5. Same as 4 except Phosphoric acid is used instead of Hydrochloric and final sol'n diluted to 200 ml	Titration		solid	Not Available	9	64

TABLE 32. TOXICITY AND COST OF GERMANE DETECTING REAGENTS

Reagents	Toxicity - Acute Local[3]	Cost - $[38,39,40]
1. Phenylfluorone	No information available	10g-19.50
2. Hydroxyphenylfluorone	No information available	Not readily available from sources checked
3. Phthalic acid; α-Naphthol; Boric acid in Sulfuric acid	Allergen 1; Irritant 2, Ingestion 3, Inhalation 1, Ingestion 2, Inhalation 2, Irritant 3, Ingestion 3, Inhalation 3	500g-10.50; 1kg-12.00; 12kg-27.00 4kg-8.50
4. Hydrochloric acid; Sodium carbonate; Potassium iodate; Potassium iodide; Starch	Irritant 3, Ingestion 3, Inhalation 3; Irritant 2, Ingestion 2, Inhalation 2; Iodates - Variable; Iodides-Ingestion 2, Inhalation 2; Allergen 1, Inhalation 1	1pt-8.50; 2kg-10.50; 500g-16.50; 100g-11.00; 1kg-14.50
5. Phosphoric acid	Irritant 2, Ingestion 2, Inhalation 2	1kg-9.00

0 NONE: (a) No harm under any conditions: (b) Harmful only under unusual conditions or overwhelming dosage.

1 SLIGHT: Causes readily reversible changes which disappear after end of exposure.

2 MODERATE: May involve both irreversible and reversible changes not severe enough to cause death or permanent injury.

3 HIGH: May cause death or permanent injury after very short term exposure to small quantities.

U Unknown-No valid information available on Humans

(1) Phenylfluorone [62]- For this approach paper is treated with 0.05 percent phenylfluorone in ethyl alcohol which has been acidified with a few drops of 6N hydrochloric acid. A solution containing germanium will then turn the paper an intense rose color. The treated paper keeps for a short time, but strongly oxidizing ions may decomp. the reagent. This method may prove valuable for the field detection of germane. Although the treated paper is not stable, under proper conditions the reagent solution is stable. We will consider this approach in our laboratory evaluation of detection systems.

(2) Hydroxyphenylfluorone [62]- This method is similar to the previous technique. It utilizes a filter paper that has been treated with 1 drop of 0.1 percent O-hydroxyphenylfluorone solution that has been slightly acidified with hydrochloric acid. The paper is dried at room temperature, and a drop of the unknown sample is placed on the paper. One to two drops of 20 percent potassium fluoride solution (in 0.5N hydrochloric acid) and 2 or 3 drops of 0.5N sulfuric acid are then placed on the paper. If germanium is present an orange color will appear, while molybdenum will produce a carmine-red color. Ceric, permanganate, and chromate ions will destroy the reagent. This approach appears promising for the detection of germane. As in the method above, modification of the procedure will more than likely be necessary before this technique can be used for our needs. We will consider this approach in conjunction with the previous technique in our laboratory research for the field detection of germane.

(3) Phthalic Acid, α-Naphthol, Boric Acid in Sulfuric Acid [63]- This method involves preparing a reagent (hydroxynaphthacenequinonesulfonic acid) with the above listed compounds. A 0.01 percent solution of this compound in concentrated sulfuric acid gives a bright pink color in the presence of germanium when viewed in a blue light. Because of the use of concentrated sulfuric acid in the field and the added accessories needed, this method will only be considered if we find that the two previously mentioned approaches inadequate.

(4) Hydrochloric Acid, Sodium Carbonate, Potassium Iodide, Potassium Iodate, Carbon Dioxide, Starch [64]- This is a titration method. It involves taking a sample containing Ge(IV) and reducing it to Ge(II) by adding hydrochloric acid and boiling. This sample is then titrated with a solution of potassium iodide, potassium iodate, and sodium carbonate, previously standardized, with a 0.1 percent starch solution as the indicator. The end point is reached when a purplish-blue color appears for a few seconds.

The method does not appear suitable for the detection of germane for several reasons. First, it is a titration method which is tedious and time consuming. Second, this method involves boiling, which means more equipment and more time. Finally, this method involves a standard solution which should be standardized daily using a titration technique. Therefore, this method will not be considered further as a method for the field detection of germane.

(5) Phosphoric Acid, Sodium Carbonate, Potassium Iodide, Potassium Iodate, Carbon Dioxide, Starch [64]- This method is approximately the same as above except phosphoric acid is used as the reducing agent. Also, the sample solution is diluted to 200ml with water and boiled for five minutes longer.

This method is also not suitable for the identical reasons given above and will not be considered further as a detection tool for germane.

HYDROGEN CYANIDE

Numerous reagent systems were discovered for the detection of hydrogen cyanide. Various information pertaining to this gas can be found in Table 33. A basic description of these different reagent systems along with their toxicity and cost can be found in Tables 34 and 35. Each of the detection reagent systems is discussed in the following sections.

Hydrogen Cyanide Detection Reagent Recommendations

The most promising detection method appears to be the Draeger detector tube (Method 13) for hydrogen cyanide. It offers good sensitivity, an incorporated interference stripping layer, and is readily available. Other commercially available detector tubes, along with the previously mentioned reagent systems, will be considered as alternative methods if Method 13 does not perform satisfactorily.

TABLE 33. PROPERTIES OF HYDROGEN CYANIDE [3,4,25,26,27]

NAME OF SUBSTANCE:	Hydrogen cyanide
MOLECULAR FORMULA:	HCN
MOLECULAR WEIGHT:	27.03
CAS REGISTRY NUMBER:	74-90-8
WISWESSER LINE NOTATION:	NCH
SYNONYM:	A. Hydrocyanic acid B. Formic anammonide C. Formonitrile D. Prussic acid E. Blausaure F. Carbon hydride nitride G. Acide cyanhydrique (French) H. Acido cianidrico (Italian) I. Aero Liquid HCN J. Blauwzuur (Dutch) K. Cyanwasserstoff (German) L. Cyjandwodor (Polish) M. HCN N. Hydrocyanic Acid, Liquefied (DOT)
MELTING POINT:	-13.4°C.
BOILING POINT:	25.6°C.
DENSITY/SPEC GRAVITY:	0.6876 g/l @ 20°C/4°C.
VAPOR PRESSURE:	630 mm Hg @ 20°C.
COLOR/FORM:	A. Colorless gas or liquid B. Colorless liquid below 26°C. C. Miscible with water, alcohol D. Miscible with ether
SOLUBILITY:	Miscible with water, alcohol and ether.
STABILITY/SHELF LIFE:	Becomes explosive with O_2 after 90 days.

(continued)

TABLE 33 (continued)

EXPLOSIVE LIMITS:	A. Explosion hazard: severe, when exposed to heat or flame or by chemical reaction with oxidizers. Under certain conditions, particularly contact with alkaline materials, HCN can polymerize or decomp. explosively.
	B. Vapor forms explosive mixt. with air may become subject to explosion if stored for extended time.
MAJOR USES:	A. Compressed gas used to exterminate rodents & insects in ships, killing insects on trees.
	B. Fumigant and nematocide
	C. Pesticide
	D. In metal polishes, electroplating solution, metallurgical & photographic processes.
	E. Mfr. of resin monomers, acrylates, methacrylates, hexamethylenediamine, nitriles; as chemical intermediate.
	F. Synthesis of chemical acrylonitrile.
	G. Intermediate for methyl methacrylate
	H. Intermediate for sodium cyanide
	I. Intermediate for aminopolycarboxylic acid chelating agents.
SPECTRAL & OTHER PROPERTIES:	A. Density: 0.941 g/l (gas) (air=1).
	B. Odor of bitter almond.
	C. Flash point -17.8°C.
	D. Lighter than air.
	E. Index of refraction: 1.2614 @ 20°C.
	F. Burns in air with blue flame.
	G. Very weakly acid (does not redden litmus).
TOXICITY VALUES:	A. LD_{50} Rabbits subcutaneous 2500 µg/kg
	B. LD_{50} Rabbits intravenous 820 µg/kg
	C. LD_{50} Rabbits intramuscular 1100 µg/kg
	D. LD_{50} Mice subcutaneous 5.8 mg/kg

(continued)

TABLE 33 (continued)

E. LD_{Lo} Frogs subcutaneous 60 mg/kg

F. LD_{Lo} Dogs intravenous 540 µg/kg

G. LD_{Lo} Rats intravenous 2500 µg/kg

H. LD_{Lo} Rats oral 10 mg/kg

I. LD_{50} Sheep oral 2.0 mg/kg

J. LD_{Lo} Mice subcutaneous 3 mg/kg

K. MAC USSR 0.3 mg/m^3

L. LD_{Lo} Dogs oral 4 mg/kg

M. LD_{Lo} Dogs subcutaneous 1700 µg/kg

N. LD_{50} Mice oral 3700 µg/kg

O. LC_{50} Dogs inhalation 339 mg/m^3/3 min.

P. LD_{50} Mice intravenous 1100 µg/kg

Q. LD_{50} Rabbits intraperitoneal 1570 µg/kg

R. LD_{50} Mice intramuscular 2700 µg/kg

S. LD_{Lo} Cats subcutaneous 1100 µg/kg

T. Aquatic toxicity: TLm: under 0.0011 mg/1/96 hrs.

U. LC_{Lo} Rabbits inhalation 2000 mg/m^3/1/2 min.

V. LC_{Lo} Cats inhalation 2500 mg/m^3/1/2 min.

W. LD_{Lo} Guinea pigs subcutaneous 100 µg/kg

X. LD_{50} Mice intraperitoneal 2990 µg/kg

Y. Max acceptable daily intake (ADI) hydrogen cyanide 0.05 mg/kg.

Z. LD_{Lo} Human oral 570 µg/kg

AA. LC_{Lo} Human inhalation 120 mg/m^3/1 hr.

BB. LC_{Lo} Human inhalation 200 mg/m^3/10 min.

CC. LD_{Lo} Human subcutaneous 1 mg/kg

DD. LD_{50} Human intravenous 1 mg/kg

EE. Toxicity rating: 6. 6=super toxic: probable oral lethal dose (human) less than 5 mg/kg, a taste (less than 7 drops) for 70 kg person (150 lb).

(continued)

TABLE 33 (continued)

FF. Toxic hazard rating: acute local: irritant 2. Acute systemic: ingestion 3; inhalation 3; skin absorption 3. 2=moderate: may involve both irreversible & reversible changes not severe enough to cause death or permanent injury. 3=high: may cause death or permanent injury after very short exposure to small quantities.

GG. So-called case of "chronic" cyanide poisoning probably represent persistent neuropsychiatric sequelae from one or more acute exposure episodes. (Cyanide)

THRESHOLD LIMIT VALUE: 10 ppm (Approx. 11 mg/m^3)- skin

PHYSIOLOGICAL EFFECTS:

A. In experimental animals, demonstration of effects of cyanide poisoning on retina & optic nerve...successful principally with acute severe, near-lethal or lethal poisonings. In acute poisoning of rabbits by sublethal doses of cyanide, changes in electroretinogram have been observed. (Cyanides)

B. Mucous membranes are pink & blood is cherry red & may not clot. Red color is due to hyperoxygenation hemorrhages on heart. GI tract & lungs may have congestion & petechial hemorrhages. (Cyanides)

C. Reacts readily with trivalent iron of /CN/ cytochrome oxidase in mitochondria to form cytochrome oxidase-CN complex, & with that of methemoglobin to form cyanmethemoglobin. When cytochrome oxidase & cyanide combine, cellular respiration is inhibited; cytotoxic hypoxia is produced.

D. Inhalation of vapors causes toxic effects & death within minutes to 3 hrs. depending upon concentration. Action is due to cyanide ion. Toxic properties of gas are shared by all soluble inorganic cyanide salts.

E. Symptoms of poisoning appear within seconds to minutes after ingestion or breathing vapors. They consist in giddiness, hypernea, headache, palpitation, cyanosis, & unconsciousness. Asphyxial convulsions may precede death.

(continued)

TABLE 33 (continued)

F. Chronic exposure to cyanides workers in electroplating indust. result in dermatitis, itching, scarlet rash, papules, irritation of nose, leading to obstruction, bleeding, sloughs, perforation of septum. (Cyanides)

G. Specific pathological finding in acute cases of cyanide poisoning is bright red color of venous blood. This is striking, visible evidence of inability of tissue cells to utilize oxygen. Venous blood is only about 1 volume % lower in oxygen content than arterial blood. (Cyanides)

H. Upon ingestion, feeling of constriction or numbness in throat. Salivation & nausea, not unusual. Paralysis follows convulsive stage. Skin is covered with sweat. Eyeballs protrude; pupils are dilated & unreactive. Mouth covered with foam. (Cyanides)

I. Only occasionally has reference been made to irritation of eye, conjunctivitis, or superficial keratitis developing after chronic exposure to hydrogen cyanide gas. (Cyanides)

MANUFACTURING INFO:

A. Preparation on large scale by catalytic oxidation of ammonia-methane mixture. May also be prepared by catalytic decomposition of formamide.

B. Prepared in laboratory by acidifying NaCN or $K_4[Fe(CN)_6]$.

C. By-product of production of acrylonitrile by catalytic oxidation of a mixt. of propylene and ammonia with air. Consumption pattern 62% as an intermediate for methyl methacrylate; 21% as an intermediate for chelating agents; 10% as an intermediate for sodium cyanide; and 7% in misc. applications (1972).

(continued)

TABLE 33 (continued)

PRODUCTION/MANUFACTURERS:		Annual Capacity (Millions of Pounds)
A. American Cyanamid Co. Indust. Chems. Div.	New Orleans, LA	32
B. Ciba-Geigy Corp. Agricultural Div.	St. Gabriel, LA	90
C. Hercules Inc. Coatings & Specialty Products Dept.	Glens Falls, NY	3
D. Degussa Corp. Alabama Group	Theodore, AL	53
E. Dow Chem. U.S.A.	Freeport, TX	20
F. E.I. du Pont de Nemours & Co., Inc. Chems. and Pigments Dept.	Memphis, TN	180
G. Petrochems, Dept.	Beaumont, TX	48
Polymer Intermediates Dept.	Orange, TX	210
	Victoria, TX	210
H. Monsanto Co.		
Monsanto Chem. Intermediates Co.	Chocolate Bayou, TX	63
	Texas City, TX	63
I. Rohm and Haas Co. Rohm and Haas Texas Inc., subsid.	Deer Park, TX	200
J. The Standard Oil Co., (Ohio) Vistron Corp., Subsid. Chems. Dept.	Lima, OH	40
	TOTAL	1,212

ENVIRONMENTAL HAZARDS:

A. angerous effects of industrial processes are: preparation of cyanides; decomp. by exposure to air & weak acids & extraction of phosphoric acid from bones. Presence of HCN in various indust. gases results from incomplete combustion of nitrogen-containing organic compounds.

B. Exposure occurs with fumigation of ships, workshops, dwellings and in fumigation intended to kill agricultural parasites; chemical laboratories, in blast-furnace gas; in Mfr. of illuminating gas; in gas from burning nitrocellulose.

(continued)

TABLE 33 (continued)

C. Factors that increase likelihood of HCN poisoning from ingestion of cyanogenic plants are large amounts of free HCN & cyanogenic glycosides, rapid ingestion of large amounts of plant, ruminal pH & microflora that continue to hydrolyze glycoside. Rapid intake of plant...equivalent to about 4 mg HCN/kg considered to be lethal. (Cyanide)

D. Since hydrogen cyanide is highly toxic to all species living in water, special attention should be given to possiblity of water pollution.

E. Breathing apparatus alone not considered complete protection in atmospheres containing over 1130 mg/m^3 - wear special protective clothing.

F. Occupational exposure to HCN recommended Std-air: ceiling 5 $mg(CN)/m^3$/10 min.

G. Std-air: time weighted average 113 mg/m^3 (skin)

H. Firefighting in advanced or massive fires: firefighting should be done from safe distance; use dry chemical, "alcohol" foam, or carbon dioxide. Water spray may be ineffective, should be used to keep fire-exposed containers cool.

I. Some identified cilia-toxic. Mucus coagulating agents in air pollutants-inorganic chemicals in tobacco smoke-hydrogen cyanide.

TABLE 34. HYDROGEN CYANIDE DETECTING REAGENTS

	Reagents	Method Matrix	Interferences	Sample Type of Matrix	Sensitivity	# of Operator Steps	Ref No.
1.	1,3-Dimethylbarbituric acid	photometric		liquid	Not Available	8	41
2.	2-Aminobenzoic acid	photometric		liquid or gas	4.0 mg/m^3	6	65
3.	p-Phenylenediamine	photometric	SCN,Zr,Cu,FeII, NiII, CuII	liquid or gas	5.0 mg/m^3	3	66
4.	Tetramethyldiaminodiphenylmethane; Copper sulfate	activated charcoal		gas	Not Available	1	67
5.	Benzidine; Copper acetate	silica gel	oxidizing materials	gas	.4 mg/m^3	1	68
6	Ferric sulfate; Ferric chloride; Potassium hydroxide	silica gel		gas	Not Available	3	69
7.	Anhydrous ferric; Ferrous sulfate	paper silica gel		liquid or gas	Not Available	1	70
8.	Copper sulfate; O-Toluidine, Sodium sulfite; Glycerol	silica gel		gas	0.075 mg (HCN)	1	71
9.	Hg^{++}-diphenylcarbazide; Sodium carbonate hydrogen	paper		gas	Not Available	1	72
10.	Gold; Mercury; Lead chloride	silica gel		gas	Not Available	1	73
11.	Sodium picrate	silica gel		gas	Not Available	1	74
12.	Chloramine T						47
13.	Draeger detection tube	silica gel		gas	2.3 mg/m^3	1	35
14.	Kitagawa detection tube	silica gel		gas	0.23 mg/m^3	1	36
15.	MSA detection tube	silica gel	NH_3, H_2S	gas	5.0 mg/m^3	1	37
16.	p-Nitrobenzaldehyde; Potassium carbonate	paper		gas	5.6 mg/m^3	1	75

TABLE 35. TOXICITY AND COST OF HYDROGEN CYANIDE DETECTING REAGENTS

Reagents	Toxicity - Acute Local[3]	Cost - $[38,39,40]
1. 1,3, Dimethylbarbituric acid	Unknown	Not readily available from sources checked
2. 2-Aminobenzoic acid	Unknown	500g-10.80
3. p-Phenylenediamine	Irritant 2, Allergen 1;	500g-21.55
4. Tetramethyldiaminodiphenylmethane; Copper sulfate	Allergen 2; Copper Compounds Ingestion 1, Irritant 1, Inhalation 1, Allergen 1; H_2SO_4-Irritant 3, Ingestion 3, Inhalation 3	11-18.35; 50g-39.00
5. Benzidine; Copper acetate	Ingestion 3, Inhalation 3, Carcinogen; Copper Compounds Irritant 1, Inhalation 1, Ingestion 1	Not readily available from sources checked; 100g-8.50
6. Ferric sulfate; Ferric chloride; Potassium hydroxide	Irritant 1; Irritant 1; Ingestion 1; Irritant 3; Ingestion 3, Inhalation 3	250g-5.65; 1kg-6.85; 100g-6.40
7. Anhydrous ferric; Ferrous sulfate	Irritant 1; Irritant 1, Inhalation 1, Ingestion 1	250g-5.65; 1kg-14.50
8. Copper sulfate; O-Toluidine; Sodium sulfite; Glycerol	Copper Compounds Ingestion 1, Inhalation 1, Allergen 1; H_2SO_4 Irritant 3, Ingestion 3, Inhalation 3, Irritant 2, Allergen 2, Ingestion 2; Sulfites Ingestion 1, Inhalation 1; Ingestion 1; O-toluidine Carcinogen	50g-39.00; 1kg-6.90; 50g-6.90; 500g-14.00

0 NONE: (a) No harm under any conditions: (b) Harmful only under unusual conditions or overwhelming dosage.

1 SLIGHT: Causes readily reversible changes which disappear after end of exposure.

2 MODERATE: May involve both irreversible and reversible changes not severe enough to cause death or permanent injury.

3 HIGH: May cause death or permanent injury after very short term exposure to small quantities.

U Unknown-No valid information available on Humans

(continued)

TABLE 35 (continued)

Reagents	Toxicity - Acute Local[3]	Cost - $[38,39,40]
9. Hg^{++}-diphenylcarbazide; Sodium carbonate hydrogen	Unknown; None	Not readily available from sources checked
10. Gold chloride; Mercury chloride; Lead chloride	Chlorides-Variable, Gold Compounds-Allergen 2, Mercury Compounds-Inhalation 3, Irritant 3, Ingestion 3; Inhalation 3; Inhalation 3	1g-23.00; 100g-40.25; 50g-43.50
11. Sodium picrate	Irritant 2, Allergen 1	Not readily available from sources checked
12. Chloramine T	Irritant 1	1kg-10.95
13. Draeger detection tube	None - Closed tube	1.00 - 2.00 each
14. Kitagawa detection tube	None - Closed tube	1.00 - 2.00 each
15. MSA detection tube	None - Closed tube	1.00 - 2.00 each
16. P-Nitrobenzaldehyde; Potassium carbonate	Unknown; Irritant 3, Ingestion 3	10g-6.60; 20g-13.75

0 NONE: (a) No harm under any conditions: (b) Harmful only under unusual conditions or overwhelming dosage.

1 SLIGHT: Causes readily reversible changes which disappear after end of exposure.

2 MODERATE: May involve both irreversible and reversible changes not severe enough to cause death or permanent injury.

3 HIGH: May cause death or permanent injury after very short term exposure to small quantities.

U Unknown-No valid information available on Humans

(1) 1,3-Dimethylbarbituric Acid [41]- This procedure consists of treating a sample (10 ml) with 10 drops each of 10 percent tartaric acid, 5 percent EDTA and 1 percent chloramine respectively. The sample is then shaken and allowed to settle for approximately 30 seconds. The sample is then treated with five drops each of 10 percent 1,3-dimethylbarbituric acid in Me_2SO and pyridine. After a 5-minute waiting period the sample is then measured at 588 nm for its cyanide concentration. This method is not as advantageous as others in terms of simplicity of operations. We will not consider this technique, because of its complexity.

(2) 2-Aminobenzoic Acid [65]- This method has a maximum detection limit of 20 µg/ml cyanide. A cyanide solution containing less than 1.13 cyanide in 0.1N sodium hydroxide is acidified with 1N hydrochloric acid and treated with bromine for 5 minutes to form bromine cyanide. Excess bromine is then reduced with ascorbic acid and after a 5-minute wait the sample is then treated with a fresh mixt. of 2-aminobenzoic acid and pyridine in dilute hydrochloric acid to form a bromide complex. After a 10-minute wait the complex is then measured at 485 nm. This technique, like the previous method, is too complex in comparison with other available methods. In addition, the sample in question must contain less than 1 mg/m^3. Therefore, the procedure is not considered suitable.

(3) p-Phenylenediamine [66]- Method 2 is considered as an alternative to this procedure due to the allergic properties of p-phenylenediamine. This method involves treating a sample with bromine water to produce bromine cyanide. The solution is then treated with p-phenylenediamine to form a complex which is then measured spectrometrically. This procedure's detection limit is 5.0 mg/m^3 with a range of from 5.0 to 100,000 mg/m^3 and has interferences of sulfur cyanide, zirconium, copper, iron, and copper. This technique is not considered promising for our purposes due to the allergic properties of the reagent, interferences, and the number of steps involved.

(4) Tetramethyldiaminodiphenylmethane and Copper Sulfate [67]- This technique utilizes a tube filled with 2 layers activated charcoal at the bottom and hydrogen cyanide-sensitive reagent on top. This reagent is prepared as follows: 1.5 g of copper sulfate are dissolved in 100ml of distilled water which is then added to 110 g of iron-free silicon dioxide. After drying, 0.1 g of tetramethydiaminodiphenylmethane and 0.5 g of benzoic acid, dissolved in 120ml of acetone, are added to the gel. In the presence of hydrocyanic acid, this reagent will turn from a pale greenish-blue to an intense blue. This procedure may prove promising, but commercial

tubes are not available. We will consider this approach in the event that current commercially available detection methods prove unsatisfactory.

(5) Benzidine and Copper Acetate [68]- The reagent for detection of hydrogen cyanide is prepared as follows: A solution of 0.2 g of benzidine in 100ml of water is heated with a few drops of acetic acid. An equal volume of a 0.3 percent solution of copper acetate is then added and mixed with 20 g of silica gel. This is a very sensitive reagent capable of detecting 0.0004mg hydrogen cyanide per 1 of air. However, the reagent is unstable and should be used within a few hrs. after preparation. This technique is not considered a promising approach due to the lack of stability of the reagent.

(6) Ferric Sulfate, Potassium Hydroxide, and Ferric Chloride [69]- This method involves aspirating an air sample through a silica gel-ferric sulfate tube. Twenty percent potassium hydroxide is then added to wet the gel, and the tube is heated. A few drops of ferric chloride in concentrated hydrochloric acid are added to give a prussian blue reaction in the presence of hydrogen cyanide. This approach is not considered promising due to the number of operator steps involved for detection.

(7) Anhydrous Ferric and Ferrous Sulfate [70]- Hydrogen cyanide can be detected by placing a drop of sample on 50 to 100mg of a mixt. of 90 percent anhydrous ferrous sulfate and 10 percent anhydrous ferric sulfate. If cyanide is present, a blue tint will appear in a few seconds. This technique may be adaptable to a detector tube but laboratory investigation would be required. It does not appear that this is one of the most promising approaches.

(8) O-Toluidine, Copper Sulfate, Sodium Sulfite, and Glycerol [71] A solution of 0.2 g of O-toluidine in 6.5ml ethyl alcohol is added to a mixt. of 0.03 g copper sulfate, 3.5ml water, 0.03 g of sodium sulfite and 2.5ml glycerol. Seven g of silica gel and 6ml ethyl alcohol is then added and the reagent is dried under vacuum. The silica gel is then placed in a glass tube under an inert atmosphere. This detector is stable for over 1 year and is sufficiently sensitive to detect 0.075 mg of hydrogen cyanide in a 5ml air sample. This reagent system appears promising, but the detector tubes are not commercially available. This method will be considered only if commercially available techniques fail.

(9) Hg^{++}-Diphenylcarbazide and Sodium Carbonate Hydrogen [72]- To detect traces of hydrogen cyanide in air, Hg^{++}-diphenylcarbazide paper is wetted with 3 percent sodium bicarbonate. To remove up to 565 mg/m^3 hydrogen sulfide and 226 mg/m^3 halogen

interferences, $Cd(NO_3)_2$, and fluorescein papers are placed before the detecting paper. In the presence of hydrogen cyanide, the detecting paper will turn pink. This method may be adaptable to a detector tube arrangement, but, as in the case above (method 8), it is currently not commercially available. This technique will only be considered if the other procedures listed prove unsatisfactory.

(10) Gold, Mercury or Lead Chloride [73]- A test tube for detecting hydrogen cyanide contains silica gel inpregnated with any one of the three chlorides. Bromothymol blue or bromocresol green is added as an indicator for hydrochloric acid. An air sample is aspirated through the tube and a color change indicates the possibility of hydrogen cyanide being present. These tubes are stable for several years. This method appears to be too interference-prone to be considered for our case. Therefore, this does not appear to be a promising technique.

(11) Sodium Picrate [74]- Silica gel is impregnated with sodium picrate dissolved in concentrated sodium hydroxide. The yellow color of the detecting reagent changes to reddish-brown in the presence of hydrogen cyanide. This procedure will not be ruled out, but, due to the fact that the tubes are not commercially available, this will only be considered as an alternative approach.

(12) Chloramine T [47]- This approach is based upon the fact that hydrogen cyanide can be readily converted to cyanogen chloride by means of chlorinating agents, such as chloramine T. Once hydrogen cyanide has been converted, its presence is determined by testing for cyanogen chloride using detecting reagents listed in this report. We do not feel that this method is as promising as other techniques, and it will not be considered in our laboratory evaluation.

(13) Draeger (No. CH 25701) [35]- The Draeger hydrogen cyanide detector tube has a range of 2.26 to 33.90 mg/m^3 when measured using five strokes of the pump. Potentially interfering acidic or basic gases, such as hydrogen sulfide, hydrogen chloride, sulfur dioxide and ammonia, are retained in a precleanse layer of the detector tube. This tube measures for hydrogen cyanide with a relative standard deviation of 10 to 15 percent. The hydrogen cyanide tube reagents have a shelf life of two years. We believe this method to be the most promising. The tubes are commercially available and contain an interference removing layer.

(14) Matheson-Kitagawa (No. 112A and 112B) [36]- Matheson has gas detector tubes for hydrogen cyanide in the measurable ranges of 1.13-113 mg/m^3/0.23-28.3 mg/m^3 (Part No. 112B) and 0.01 to 3 percent (Part No. 112A). The 112A tube requires one pump

stroke and lists acetone, hydrogen sulfide and sulfur dioxide as interferences. This tube has a shelf life of 1.5 years. The 112B detector tube requires one stroke for the first measurable range and four strokes for the second measurable range. This tube has a shelf life of one year and interferences are listed as ammonia, chloride, hydrogen sulfide and sulfur dioxide. The detection tube appears to be a good candidate if a precleanse layer is used to eliminate interferences.

(15) MSA (No. 93262) [37]- The MSA gas detector tube for hydrogen cyanide (93262) has a measurable range of 90-40 mg/m^3. Ammonia and hydrogen sulfide are listed as interferences with the detector tube. A precleanse layer is needed to eliminate interferences, but this method will be considered as an alternative approach.

(16) p-Nitrobenzaldehyde and Potassium Carbonate [75]- A test paper is treated with a mixt. of p-nitrobenzaldehyde (in diacetone alcohol) and potassium carbonate. A reddish-purple color is obtained upon exposure of the paper to an atmosphere containing 10.3 mg/m^3 hydrogen cyanide. The reagent is stable and no interference is caused by the presence of a few hundred mg/m^3 of chlorine, ammonia, or nitrogen peroxide. The sensitivity of this method is 6 mg/m^3. This method is not as advantageous as the commercially available techniques, but will remain as another feasible detection method.

LEWISITE

Eleven potential field screening methods were found for the detection of lewisite. Table 36 gives various information pertaining to this compound while Tables 37 and 38 describe various aspects of the eleven reagent systems. A short description of these systems is given in the following sections.

Lewisite Detection Reagent Recommendations

The most promising method for the field detection of lewisite appears to be the use of Michler's thioketone reagent system. The method appears to be relatively specific for lewisite. No information was available as to the reagent sensitivity; this will have to be determined in the laboratory. However, this method is expected to be fairly sensitive since this is the method of choice used by the United States Army in the M-256 War Gas Detection Kit for the detection of lewisite. It would also appear that the shelf life of the detecting reagent is acceptable since it is already used in a kit.

TABLE 36. PROPERTIES OF LEWISITE [3,4,25,26,27]

NAME OF SUBSTANCE:	Lewisite
MOLECULAR FORMULA:	$C_2H_2AsCl_3$
MOLECULAR WEIGHT:	207.31
CAS REGISTRY NUMBER:	541-25-3
WISWESSER LINE NOTATION:	G1U1-AS-GG
SYNONYMS:	A. Arsine, (2-chlorovinyl-dichloro-) B. Arsonous dichloride, (2-chloroethenyl)- (9CI) C. Chlorovinylarsine dichloride D. 2-Chlorovinyldichloroarsine E. Beta-chlorovinylbichloroarsine F. Dichloro(2-chlorovinyl)arsine G. Arsine, Dichloro(2-chlorovinyl)-
MELTING POINT:	0.1°C
BOILING POINT:	190°C (decomposition)
DENSITY/SPEC GRAVITY:	1.888 g/l
VAPOR PRESSURE:	0.395mm Hg at 20°C
COLOR/FORM:	Liquid
SOLUBILITY:	A. Insoluble in water B. Soluble in ordinary organic solvents.
STABILITY/SHELF LIFE:	No information available
EXPLOSIVE LIMITS:	No information available
MAJOR USES:	A. Vesicant B. War gas C. Respiratory and systemic poison
SPECTRAL AND OTHER PROPERTIES:	A. Faint odor of geranium B. Hydrolyzed by alkalies C. Neutralized and inactivated by bleaching powder, sodium hypochlorite.

(continued)

TABLE 36 (continued)

TOXICITY VALUES:	A. LD_{50} Skin of rat 24 mg/kg
	B. LD_{50} Subcutaneous rat 1 mg/kg
	C. LC_{Lo} Inhalation mouse 150 mg/m^3/10 min.
	D. LD_{50} Skin of dogs 2 mg/kg
	E. LD_{50} Skin of rabbit 6 mg/kg
	F. LD_{50} Subcutaneous rabbit 2 mg/kg
	G. LD_{50} Intravenous rabbit 500 µg/kg
	H. LD_{50} Oral rat 50 mg/kg
	I. LD_{Lo} Skin of humans 20 µg/kg
	J. LC_{Lo} Inhalation humans 50.8mg/m^3/30 min.
THRESHOLD LIMIT VALUE:	No information available
PHYSIOLOGICAL EFFECTS:	A. Produces severe vesication
	B. Produces severe systemic effects
	C. Is absorbed through skin
	D. Has delayed action
	E. Irritating effects on the eyes and mucous membranes of mouth and nose.
MANUFACTURING INFO:	A. Manufactured by passing acetylene into a mixt. of arsenic trichloride and aluminum chloride.
	B. Prepared by the reduction of the corresponding arsenic or arsonic acid by sulfur dioxide in the presence of hydrochloric or hydrobromic acid and with the addition of a trace of potassium iodide.
PRODUCTION:	No information available
MANUFACTURERS:	Not commercially available
ENVIRONMENTAL HAZARDS:	No information available

TABLE 37. LEWISITE DETECTING REAGENTS

	Reagents	Method Matrix	Interferences	Sample Type of Matrix	Sensitivity	# of Operator Steps	Ref No.
1.	Methyl orange; Amyl alcohol	solution	acid	gas	Not Available	1	76
2.	Sodium hydroxide; Cuprous chloride	solution	acetylene	gas	Not Available	3	42
3.	Osmic acid	silica gel	Acrolein	gas	25 mg /m^3-4L sample	1	77
4.	Ergosterol	silica gel	HCL - diff. color	gas	Not Available	1	78
5.	Cupric carbonate; Arsenic trioxide	colorimetric		gas or liquid	Not Available	1	79
6	Sodium carbonate; Potassium iodide	colorimetric	any arsenic comp.	gas or liquid	Not Available	3	80
7.	Fluorescein; Fuchsin; Mercurochrome	paper		gas or liquid	0.003 mg	1	52
8.	Mercurous chloride	silica gel	arsenic compounds	gas	Not Available	1	81
9.	Michler's thioketone	crayon			Not Available	1	47
10.	Ilosvay reagent	silica gel		liquid or gas	Not Available	2	82
11.	Sodium hydroxide; Tin Chloride-Hydrochloric acid solution	silica gel		gas	Not Available	3	83

TABLE 38. TOXICITY AND COST OF LEWISITE DETECTING REAGENTS

Reagents	Toxicity - Acute Local[3]	Cost - $[38,39,40]
1. Methyl orange; Amyl alcohol	Unknown; Irritant 2, Inhalation 2	25g-4.35; 1g-6.50
2. Sodium hydroxide; Cuprous chloride	Irritant 3, Ingestion 3, Inhalation 2; Copper Compounds Irritant 1; Ingestion 1; Inhalation 1	500g-6.40; 500g-9.50
3. Osmic acid	Irritant 3, Inhalation 3	40ml-32.90
4. Ergosterol	None	25g-8.50
5. Cupric carbonate; Arsenic trioxide	Copper Compounds-Irritant 1, Ingestion 1, Inhalation 1, Arsenic Compounds - Irritant 2, Allergen 2, Ingestion 3	500g-24.50; 5g-6.00
6. Fluorescein; Fuchsin; Mercurochrome	Allergen 1; Unknown Possible Carcinogen; Ingestion 3; Irritant 1	100g-5.05; 100g-45.35; 25g-8.15
7. Mercurous chloride	*Mercury Compounds*-Irritant 3, Inhalation 2, Ingestion 3; Chlorides-Variable	100g-15.50
8. Sodium carbonate; Potassium iodide	Irritant 2, Ingestion 2, Inhalation 2; Iodides-Variable	20g-33.00; 50g-39.00
9. Michler's thioketone (4,4'-bis(dimethylamino)thiobenzophenone)	Ingestion 1	10g-22.00

0 NONE: (a) No harm under any conditions: (b) Harmful only under unusual conditions or overwhelming dosage.

1 SLIGHT: Causes readily reversible changes which disappear after end of exposure.

2 MODERATE: May involve both irreversible and reversible changes not severe enough to cause death or permanent injury.

3 HIGH: May cause death or permanent injury after very short term exposure to small quantities.

U Unknown-No valid information available on Humans

(continued)

TABLE 38 (continued)

Reagents	Toxicity - Acute Local	Cost - $[38,39,40]
10. Ilosvay reagent	Unknown	Not readily available from sources checked
11. Sodium hydroxide; Tin chloride - Hydrochloric acid solution	Irritant 3, Ingestion 3, Inhalation 2; Irritant 3, Ingestion 3, Inhalation 3	500g-6.40; 10g-17.25

0 NONE: (a) No harm under any conditions: (b) Harmful only under unusual conditions or overwhelming dosage.

1 SLIGHT: Causes readily reversible changes which disappear after end of exposure.

2 MODERATE: May involve both irreversible and reversible changes not severe enough to cause death or permanent injury.

3 HIGH: May cause death or permanent injury after very short term exposure to small quantities.

U Unknown-No valid information available on Humans

(1) Methyl Orange and Amyl Alcohol [76] - A 0.05 percent methyl orange in amyl alcohol solution is the reagent for this test. A sample is bubbled through the mixt. and a red color develops in the presence of aliphatic arsines, such as lewisite. Mustard gas, also a Class A poison, interferes with the reaction. This method is based entirely on an acid-base reaction and would be far too prone to interference problems to be considered practical.

(2) Sodium Hydroxide [42] - This method identifies lewisite by its decomposition products, which give reactions for acid, chloride, and arsenic. A gas sample is bubbled through 1 ml of a 15 percent sodium hydroxide solution; if lewisite is present, it decomp. The acetylene formed will produce a red stain on cuprous chloride test paper while the arsenic will give a direct Gutzeit test. This method is not considered a promising approach due to interference problems and the number of operator steps.

(3) Osmic Acid [77] - For this method lewisite is adsorbed onto silica gel in a tube and a few drops of osmic acid are added to the detector. If lewisite is present, a black ring of osmium dioxide will appear. This technique can detect 25 mg/m^3 of lewisite if a 4 liter sample is used. Vapors of ethyl alcohol, ethyl ether, acetone, or sulfur dioxide do not interfere as long as the concentration of lewisite is less than 4 mg/m^3. Acrolein, a super toxic compound (< 5mg fatal), does interfere with this method. This technique does not offer the specificity desired, but will be considered if other more promising methods fail to perform adequately.

(4) Ergosterol [78] - For this procedure silica gel is impregnated with a chloroform solution of ergosterol. When a gas sample containing lewisite is brought into contact with the treated gel, a violet color immediately appears which changes to a deep green with larger amounts of the vapor. If the vapor of hydrochloric acid is present, the reagent color changes to a deep rust brown. This approach will be considered as an alternative technique.

(5) Cupric Carbonate and Arsenic Trioxide [79] - This technique is based upon the reaction of cuprous ions, in aqueous alkaline solution, turning brownish-red in the presence of lewisite. The reagent is produced by pulverizing 0.2 grams of cupric carbonate and 12 grams of arsenic trioxide and adding this,along with 1 ml of piperidine, to 100 ml of water. The piperidine is added because it will change the brownish-red color to a more brilliant red. The sample in question is then introduced to the reagent, and a red color indicates the presence of lewisite. This method has the disadvantage of using arsenic trioxide, an EPA priority pollutant. Therefore, waste

generated during testing by this method may present a problem. We will consider a replacement for the arsenic trioxide if we discover that other lewisite detection methods are not satisfactory.

(6) Sodium Carbonate and Potassium Iodide [80] - This procedure detects the arsenic in lewisite and by mineralization of the organic arsenic by a sodium carbonate solution. The arsenic is then oxidized by an iodine-potassium iodide solution. Arsenomolybdate formation can then occur. This is reduced to molybdenum blue which is determined colorimetrically. This method takes approximately 15 minutes to conduct. This method does not appear promising due to the length of time required to perform the test and the lack of specificity.

(7) Fluorescein, Fuchsin, and Mercurochrome [52] - Micro-amounts of lewisite can be detected by impregnating filter paper with 0.01 percent fluorescein, 0.1 percent of fuchsin, and 0.5 percent mercurochrome. The paper can detect as little as 0.003mg of lewisite in common organic solvents. This procedure will be considered as an alternative to method 9 should the latter prove unacceptable.

(8) Mercurous Chloride [81] - Lewisite is detected in an indicator tube in which arsenic derivatives are first adsorbed and then hydrolyzed on an activated alkaline surface. The arsenites are then reduced to arsine by nascent hydrogen, generated by breaking a hydrochloric acid containing capillary in the presence of metal filings. This is then drawn into an indicator zone containing mercurous chloride, which gives a specific visible reaction. This method does not appear promising in comparison to other available techniques.

(9) Michler's Thioketone [47] - This procedure uses a crayon for the detection of lewisite. The crayon is produced by completely adsorbing, on blanc fixe, a benzene - chloroform solution of 4,4'-bis(dimethylamino)-thiobenzophenone (Michler's thioketone). This solvent is completely evaporated and the powder is pressed into crayons. The crayon is made up to contain 5 percent Michler's thioketone and 95 percent blanc fixe.

The light tan marks made by this crayon will turn an intense green-blue on contact with lewisite. Ethyl dichloroarsine also produces a green-blue coloration, while, in high concentration, phosgene will turn the crayon mark purple. Chlorine and cyanogen bromide cause the marks to become grayish in color. This reagent can also be adsorbed onto silica gel for testing purposes. We believe that this is the most promising method for the field detection of lewisite. The U.S. Army utilizes this technique for the detection of this substance in their M256 War Gas Detector Kit.

(10) Ilosvay Reagent [82] - Due to the instability of Ilosvay reagent, the reagents for this procedure are dissolved individually. Each of the components - 3 g of copper sulfate, 3 g of ammonium chloride, 5 g of hydroxylamine hydrochloride, and 4ml of concentrated ammonium hydroxide are dissolved in 25ml of water. At the time of the test one drop of each of these solutions is mixed to prepare the reagent. One drop of this is added to two drops of 20 percent potassium hydroxide; a fraction of this mixt. is then introduced to silica gel which contains the sample in question. If lewisite is present the silica gel will turn a characteristic purple. This technique will be considered as an alternative approach.

(11) Sodium Hydroxide, Tin Chloride - Hydrochloric Acid Sol'n [83] - A sample of air is aspirated through a silica gel tube for this method. A few drops of 10 percent sodium hydroxide are then added to the tube which is then heated with a match. A tin chloride - hydrochloric acid solution is added to the tube producing a black-brown precipitate if lewisite is present. This does not appear to be a promising method due to the number of operator steps and probable interference problems.

NITRIC OXIDE

Six methods were located for the detection of this gas. The physical, chemical, toxicological, and other criteria dealing with this gas are found in Table 39. Information pertaining to the six detection methods is located in Tables 40 and 41. Each of the detection methods is discussed in the following sections.

Nitric Oxide Detection Reagent Recommendations

The most promising technique for the detection of nitric oxide appears to be the Draeger combination detection tube (Method 6) for nitric oxide and nitrogen dioxide. Since the latter gas is also a Class A poison, both gases can be screened simultaneously. If this procedure proves unsatisfactory in the laboratory, other commercially available detector tubes will be examined.

TABLE 39. PROPERTIES OF NITRIC OXIDE[3,4,25,26,27]

NAME OF SUBSTANCE:	Nitric oxide
MOLECULAR FORMULA:	NO
MOLECULAR WEIGHT:	30.01
CAS REGISTRY NUMBER:	10102-43-9
WISWESSER LINE NOTATION:	No information available
SYNONYMS:	A. Mononitrogen monoxide B. Nitrogen monoxide C. Bioxyde d'azote (French) D. Oxyde nitroque (French) E. Stickmonoxyd (German) F. Nitrogen oxide (NO)
MELTING POINT:	-163.6°C
BOILING POINT:	-151.7°C
DENSITY/SPEC GRAVITY:	1.27 g/l @ -150.2°C liquid
VAPOR PRESSURE:	760 mm Hg @ - 151°C
COLOR/FORM:	A. Colorless gas B. Deep blue when liquid: bluish-white snow when solid.
SOLUBILITY:	A. 7.34 ml/100 ml water @ 0°C B. 3.4 ml/100 ml sulfuric acid C. 26.6 ml/100 ml alcohol D. Soluble in carbon disulfide, iron sulfate E. 4.6 ml/100 ml water @ 20°C, 1 atm
STABILITY/SHELF LIFE:	No information available
EXPLOSIVE LIMITS:	A. Mixt. of nitric oxide & ozone explodes even when quantity of ozone is small. B. Mixt. of nitric oxide & chlorine monoxide can be explosive.
MAJOR USES:	Manufacturing of nitric acid, in bleaching of rayon; stabilizer for propylene, methyl ether.

(continued)

TABLE 39 (continued)

SPECTRAL & OTHER PROPERTIES:	A. Combines with oxygen to form NO_2 (brown gas) & with chlorine & bromine to form nitrosyl halides, such as NOCl.
	B. Can react vigorously with reducing materials
	C. Vapor density (gas): 1.04 g/l (air=1)
	D. Trouton constant: 27.1
	E. Heat of formation: -21.5 kcal/mol @ 18°C
	F. Heat of vaporization: 3.293 kcal/mol
	G. Critical temp: -94°C
	H. Critical pressure: 65 atm
TOXICITY VALUES:	A. LC_{50} Rabbits inhalation 394 mg/m^3/15 min.
	B. LC_{50} Mice inhalation 400 mg/m^3.
	C. Data indicate that NO is about 1/5 as toxic as NO_2. Assuming minimal contamination with NO_2 & no synergistic action.
	D. Acute local: irritant 3. acute systemic: inhalation 3. 3=high: may cause death or permanent injury after very short exposure to small quantities.
	E. Chronic systemic: inhalation 2. 2=moderate: may involve both irreversible & reversible changes not severe enough to cause death or permanent injury.
THRESHOLD LIMIT VALUE:	Air: 31.25 mg/m^3
PHYSIOLOGICAL EFFECTS:	A. Chief toxic effect of nitric oxide has been ascribed to formation of methemoglobin & subsequent action on CNS.
	B. Usually nitric oxide symptoms occur @ time of exposure, with exception of slight cough, fatigue & nausea.
	C. At very high concentrations, nitrous fumes produce prompt coughing, choking, headache, nausea, abdominal pain, dyspnea.
	D. Symptom-free period follows & lasts for 5-72 hours.

(continued)

TABLE 39 (continued)

MANUFACTURING INFO:

A. Prepared industrially by passing air through electric arc (basis of atmospheric nitrogen fixation) or by oxidation of ammonia over platinum gauze.

PRODUCTION: No information available

MANUFACTURERS: No information available

ENVIRONMENTAL HAZARDS:

A. Immediately on contact with air, nitric oxide is converted to highly poisonous nitrogen dioxide, nitrogen tetroxide or both.

B. When heated to decomposition, it emits highly toxic fumes of NO (X); will react with water or steam to produce heat & corrosive fume.

C. In most urban areas the car is single largest producer of nitric oxide, which moves so rapidly from engine cylinder to cooler exhaust pipes that it is prevented from decomp.

D. In terms of amount of material emitted annually into air, five major pollutants account for close to 98% of pollution. These are nitrogen oxides.

E. Gas masks plus adequate ventilation are mandatory when handling even small amounts in lab.

F. Std air: time weighted average 31.25 mg/m^3.

G. Basic ventilation methods are local exhaust ventilation & dilution or general ventilation.

H. Nitric oxide is converted spontaneously in air to nitrogen dioxide, hence some of latter gas is invariably present whenever nitric oxide is found in air. At concentrations below 62.5 mg/m^3 this reaction is slow & frequently substantial, concentrations of NO may occur with negligible quantities of NO_2.

I. Nitric oxide will burn with nearly all fuels which will burn with air.

J. Phosphine plus nitric oxide can be ignited by addition of oxygen.

K. Rubidium carbide ignites on warming in sulfur dioxide or nitric oxide vapor.

TABLE 40. NITRIC OXIDE DETECTING REAGENTS

Reagents	Method Matrix	Interferences	Sample Type Matrix	Sensitivity	# of Operator Steps	Ref No.
1. Copper	Colorimetric		air	Not Available	3	84
2. Potassium nitrodisulfonate	Photometric		air	Not Available	5	85
3. Sulfanilic acid; 1-Naphthylamine	Colorimetric		air	Not Available	7	86
4. Matheson-Kitagawa detection tube	Silica gel	Chlorine, Ozone	air	12.3 mg/m^3	2	36
5. MSA detection tube	Silica gel	Halogens, H_2S	air	1.23 mg/m^3	2	37
6. Draeger (NO & NO_2), (NO_2)	Silica gel	Ozone, Chlorine	air	0.62 mg/m^3	4	35

TABLE 41. TOXICITY AND COST OF NITRIC OXIDE DETECTING REAGENTS

Reagents	Toxicity - Acute Local[3]	Cost - $[38,39,40]
1. Copper	Irritant 1, Allergen 1, Ingestion 1, Inhalation 1	10g-24.00
2. Potassium nitrosulfonate	No information available	10g-30.75
3. Sulfanilic acid; 1-Naphthylamine	Unknown, Ingestion 3, Inhalation 3, Skin Absorption 3	100g-0.25-9.59, 100g-14.00
4. Matheson-Kitagawa detection tube	Closed tube	1.00-2.00 - 1 tube
5. MSA detection tube	Closed tube	1.00-2.00 - 1 tube
6. Draeger detection tube	Closed tube	1.00-2.00 - 1 tube

0 NONE: (a) No harm under any conditions: (b) Harmful only under unusual conditions or overwhelming dosage.

1 SLIGHT: Causes readily reversible changes which disappear after end of exposure.

2 MODERATE: May involve both irreversible and reversible changes not severe enough to cause death or permanent injury.

3 HIGH: May cause death or permanent injury after very short term exposure to small quantities.

U Unknown-No valid information available on Humans

(1) Copper [84]- This technique involves reacting nitric oxide with reduced copper in wire form at 600°C. This reaction produces cuprous oxide which then can be determined colorimetrically. The procedure does not appear satisfactory for field screening purposes and will not be considered further.

(2) Potassium Nitrodisulfonate [85]- This procedure involves dissolving 1 g of potassium nitrodisulfonate in 35ml of 1N sodium hydroxide. This solution is then added to an air sample that contains nitric oxide. This mixture is then shaken until it becomes colorless. The amount of nitric oxide absorbed is then measured photometrically. This method also does not appear promising in comparison to other reagent systems examined.

(3) Sulfanilic Acid and 1-Naphthylamine [86]- This procedure calls for the gas sample to be scrubbed in 30 percent potassium hydroxide to remove hydrogen sulfide, nitrogen dioxide and sulfur dioxide. The gas is then rescrubbed with 5 percent potassium permanganate and sulfuric acid which oxidize the nitric oxide to nitrogen dioxide. The nitrogen dioxide is then determined colorimetrically in a solution of 1 percent sulfanilic acid and 0.4 percent 1-naphthylamine.

This technique may be adaptable to a detector tube approach and will be considered an alternative technique if current commercially available detecting systems prove unsatisfactory.

(4) Matheson-Kitagawa (No. 174) [36]- Matheson markets a detector tube which can measure a range of 12.5-3750 mg/m^3 using one pump stroke. This tube has a shelf life of approximately 1 year. Chlorine, nitrogen dioxide and ozone are given as interferences with this tube. A separate pre-treat tube is available with this detector tube which allows for the measurement of nitrogen dioxide. This method appears comparable to Method 6 and will be considered as an alternative method.

(5) MSA (No. 460425) [37]- The nitric oxide detector tube distributed by MSA measures 1.25-187.5 mg/m^3 nitric oxide. Halogens and H_2S are listed as interferences with this tube. This appears to be a promising technique and will be considered as an alternative test.

(6) Draeger [35]- Draeger does not make a gas detection tube for nitric oxide . However, they do make a gas detection tube for nitrogen dioxide and a tube for nitric oxide and nitrogen dioxide combined. Thus, nitric oxide may be obtained by the difference in the reading of the two types of tubes. It would appear that an accuracy with a standard deviation of 10 to 15 percent might be achieved using this technique. Ozone and

chlorine interfere in that they react like nitrogen dioxide. This tube has a shelf life of two years. This method of combining two detector tubes appears to be the most promising approach.

NITROGEN DIOXIDE

The physical and chemical properties of nitrogen dioxide are given in Table 42. Also included in this table are data pertaining to the toxicological properties as well as to its manufacture. Tables 43 & 44 contain a summary of information concerning each of the detection reagent systems. The toxicity and price of each reagent systems are discussed in detail in the following sections.

Nitrogen Dioxide Detection Reagent Recommendations

There are three commercially available colorimetric detection methods for nitrogen dioxide (Methods 10, 11, and 12). The most promising of these appears to be Method 12. The other two methods will be reserved as alternatives.

Method 12 utilizes the Draeger tube (No. 29401) which detects both NO and NO_2. Thus, this tube can be used to concurrently screen for both Class A poisons. The tube has a shelf life of approximately two years and the only listed interferences are ozone and chlorine.

TABLE 42. PROPERTIES OF NITROGEN DIOXIDE [3,4,25,26,27]

NAME OF SUBSTANCE:	Nitrogen dioxide
MOLECULAR FORMULA:	NO_2
MOLECULAR WEIGHT:	46.01
CAS REGISTRY NUMBER:	10102-44-0
WISWESSER LINE NOTATION:	ONO
SYNONYMS:	A. Nitrogen oxide (NO_2) B. Nitrogen tetroxide C. Nitrito D. Nitro E. Nitrogen dioxide (NO_2) F. Nitrogen peroxide G. Azote (French) H. Azoto (Italian) I. Stickstoffdioxid (German) J. Stikstofdioxyde (Dutch)
MELTING POINT:	-9.3°C
BOILING POINT:	21.15°C
DENSITY/SPEC GRAVITY:	1.448 g/l @ 20°C/4°C (Liquid)
VAPOR PRESSURE:	400 mm Hg @ 80°C
COLOR/FORM:	Yellow liquid, brown gas, reddish-brown gas.
SOLUBILITY:	A. Soluble in water with decomposition B. Soluble in alkalies, chloroform, carbon disulfide C. Soluble in concentrated sulfuric acid, nitric acid.
STABILITY/SHELF LIFE:	No information available
EXPLOSIVE LIMITS:	A. Violent reaction with cyclohexane, fluorine, formaldehyde & alcohol nitrobenzene, petroleum, toluene. B. Reactions between nitrogen tetroxide, both ordinary fuels & rocket fuels; & between

(continued)

TABLE 42 (continued)

nitrogen tetroxide & most chlorinated hydrocarbons, may be violent.

MAJOR USES:

A. Intermediate in nitric and sulfuric acid productions; has been used to bleach flour.

B. Nitration of organic compounds & explosives; mfr. of oxidized cellulose compound (hemostatic cotton)

C. Chemical intermediate (captive) for nitric acid.

D. Catalyst for sulfuric acid (chamber process)

E. Oxidizing agent for rocket fuels & fuels for high performance cars; polymerization inhibitor for acrylates.

SPECTRAL & OTHER PROPERTIES:

A. Critical temperature: 158.2°C; critical pressure: 99.96 atm

B. Liquid below 21.15°C

C. Density (gas): 1.58 g/l (air=1), 3.3 g/l @ 21.3°C/gas

D. Heat of vaporization (BP) 9.110 kcal/mol; decomposition in water forming nitric acid & nitric oxide.

E. Reacts with alkalies to form nitrates & nitrites.

F. Index of refraction: 1.40 @ 20°C

TOXICITY VALUES:

A. LC_{50} Rats inhalation 169 mg/m^3/4 hrs.

B. LC_{Lo} Mice inhalation 480 mg/m^3/30 min.

C. LC_{Lo} Monkeys inhalation 84 mg/m^3/6 hrs.

D. LC_{50} Rabbits inhalation 605 mg/m^3/15 min.

E. Cats showed severe symptoms but recovered after 4 hrs. exposure to 50 ppm (100 mg/m^3).

F. Cats showed fatal responses after 2-3 hrs. exposure to 100 ppm (210 mg/m^3), after 1/2 hr exposure to 200 ppm (420 mg/m^3) and after 13 min. exposure to 2,000 ppm (4260 mg/m^3).

(continued)

TABLE 42 (continued)

G. Pulmonary edema may not develop for up to 72 hours after exposure. Time between exposure & onset of edema is usually free of symptoms. Greatest hazard is due to length of time that passes after exposure, even though dangerous amounts have been inhaled.

H. LC_{LO} Human inhalation 384 mg/m^3/1 min.

THRESHOLD LIMIT VALUE: 5 ppm (Approx. 9 mg/m^3), 1971.

MANUFACTURING INFO:

A. Prepared industrially from nitric oxide & air.

B. Convenient lab preparation from lead nitrate.

PRODUCTION: (1972) - $4.54X10^5$ grams - in U.S.

MANUFACTURERS: Air Products and Chems, Inc., Specialty Gas Dept., Hometown, PA 18252.

ENVIRONMENTAL HAZARD:

A. Ordinary type A (acid gas) or type AB (acid gas & organic vapor) canister gas masks, with soda lime or soda lime-activated carbon fills, do not offer satisfactory protection against nitrogen dioxide gas.

B. May cause fire on contact with clothing, other combustible materials. Supports combustion of carbon, phosphorous, sulfur.

C. Violent reaction with cyclohexane, F_2, formaldehyde, alcohols, nitrobenzene, petroleum and toluene.

TABLE 43. NITROGEN DIOXIDE DETECTING REAGENTS

Reagents	Method Matrix	Interferences	Sample Type Matrix	Sensitivity	# of Operator Steps	Ref No.
1. Benzidine	Colorimetric		air	Not Available	2	54
2. Diphenylamine	Water on NaOH		air	Not Available	3	76
3. O-Tolidine chloride	Silica granules		air	0.96 mg/m^3	1	55
4. Rivanol; Potassium bisulfate	Silica gel	Chlorine, Iodine, H_2S, SO_2, CO_2, CO, and ammonia	air	4.0 mg/l	1	56
5. P-Anisidine	Paper	ozone	air	0.6 mg/m^3	1	57
6. N,N,N',N'-Tetraphenylbenzidine	Silica gel		air	Not Available	1	87
7. Potassium iodide; Potassium permanganate; Starch; Hyposulfite	Silica gel		air	Not Available	1	88
8. Potassium iodide; Sulfanilic acid; 1-Naphthylamine	Potassium iodide soln		air	Not Available	3	89
9. Alkaline iodide	Titration		air	Not Available	3	90
10. Matheson-Kitagawa (117 & 117B)	Silica gel	HCl, SO_2	air	1.92 mg/m^3	2	36
11. MSA	Silica gel	Hydrogen sulfide halides	air	0 mg/m^3	2	37
12. Draeger (CH29401)	Silica gel	Ozone, chlorine	air	0.96 mg/m^3 3.84 mg/m^3	3	35

TABLE 44. TOXICITY AND COST OF NITROGEN DIOXIDE DETECTING REAGENTS

Reagents	Toxicity - Acute Local[3]	Cost - $[38,39,40]
1. Benzidine	Ingestion 3, Inhalation 3, skin absorption 3, Carcinogen	Not readily available from sources checked
2. Diphenylamine	Ingestion 3, Inhalation 3, skin absorption 3	200g-11.50
3. O-Tolidine chloride	No information available, Carcinogen	Not readily available
4. Rivanol; Potassium bisulfate	Irritant 2, Ingestion 2, Inhalation 2, Sulfates-Variable	5g-8.50; 2g-21.00
5. P-Anisidine	Irritant 2, Allergen 1, Ingestion 2	100g-14.50
6. N,N,N',N',-Tetraphenylbenzidine	No information available, possible Carcinogen	Not readily available from sources checked
7. Potassium iodide; Potassium permanganate; Starch; Hyposulfite	Iodides-Ingestion 2, Inhalation 2; Irritant 3, Ingestion 3, Inhalation 3; Allergen 1, Inhalation 1; Sulfites Ingestion 2, Inhalation 2	500g-16.50; 2g-19.50; 1kg-14.50 2kg-8.50
8. Potassium iodide; Sulfanilic acid, 1-Naphthylamine	Iodides-Ingestion 2, Inhalation 2; unknown; Ingestion 3, Inhalation 3, Skin Absorption	500g-16.50; 100g-0.25-9.50 100g-14.50
9. Alkaline iodide	Irritant 3, Ingestion 3, Inhalation 2	2kg-12.00

0 NONE: (a) No harm under any conditions: (b) Harmful only under unusual conditions or overwhelming dosage.

1 SLIGHT: Causes readily reversible changes which disappear after end of exposure.

2 MODERATE: May involve both irreversible and reversible changes not severe enough to cause death or permanent injury.

3 HIGH: May cause death or permanent injury after very short term exposure to small quantities.

U Unknown-No valid information available on Humans

(continued)

TABLE 44 (continued)

Reagents	Toxicity - Acute Local[3]	Cost - $[38,39,40]
10. Matheson-Kitagawa detection tube	Closed tube	1.00-2.00 1 tube
11. MSA detection tube	Closed tube	1.00-2.00 1 tube
12. Draeger detection tube	Closed tube	1.00-2.00 1 tube

0 NONE: (a) No harm under any conditions: (b) Harmful only under unusual conditions or overwhelming dosage.

1 SLIGHT: Causes readily reversible changes which disappear after end of exposure.

2 MODERATE: May involve both irreversible and reversible changes not severe enough to cause death or permanent injury.

3 HIGH: May cause death or permanent injury after very short term exposure to small quantities.

U Unknown-No valid information available on Humans

(1) Benzidine [54]- This compound, after exposure to nitrogen dioxide, will couple with b-naphthol to produce a red dye material. This method is not commercially available. Also, benzidine is a highly carcinogenic compound. This method does not seem very promising, therefore it will not be examined further.

(2) Diphenylamine [76]- This detection method involves mixing an air sample with either water or sodium hydroxide. Several drops of reagent, containing 1 to 2 g of diphenylamine dissolved in 50 ml of water and 50 ml of concentrated sulfuric acid added dropwise, are added to the sample. If nitrogen dioxides are present, a blue color will develop in the solution.

This method is not commercially available as a colorimetric detection kit. The reagents utilized are also highly toxic. This method will not be studied further unless the commercially available methods are found to be unacceptable.

(3) o-Tolidine Chloride [55]- A possible Kitagawa detector tube is used for this method for determining nitrogen dioxide in air samples. The tube consists of silica granules on which o-tolidine chloride has been adsorbed and dried. Nitrogen dioxide gas reacts with the o-tolidine chloride to produce a greenish-yellow color. The limit of detection of this procedure is about 0.096 mg/m^3.

This method utilizes o-tolidine chloride which is a carcinogen and is not readily available from sources checked.

(4) Rivanol and Potassium Bisulfate [56]- This technique also utilizes gas detector tubes. Rivanol and potassium bisulfate are impregnated onto silica gel which is then placed into suitable adsorption tubes. The sample is aspirated through the tubes and, in the presence of small quantities of nitrogen dioxide, a pale pink coloration is formed; higher concentrations will produce a red coloration. The sensitivity is sufficient to accurately determine between 4.0 to 100 mg/m^3. Chlorine, iodine, hydrogen sulfide, sulfur dioxide, carbon dioxide, carbon monoxide and ammonia in low concentrations do not interfere with this test.

This method is not commercially available as a colorimetric detector kit. Although this method is very sensitive, there are methods that are commercially available that are just as sensitive and these will be tried first. If the commercially available methods prove unsuitable, then this method will be considered.

(5) p-Anisidine [57]- A detector paper, impregnated with 12 percent p-anisidine in methanol, is used for this test. The paper changes from light yellow to red-brown when air containing nitrogen dioxide is drawn through it. The paper, which gradually deteriorates in storage, can detect 0.6 mg/m^3 of nitrogen dioxide when a 50 ml air sample is used. Ozone interferes with this test, but $\leq$ 0.4 mg of hydrogen chloride and $\leq$ 0.18 mg of sulfur dioxide do not.

This method is not commercially available as a colorimetric detection method. There is also an interference from ozone which would require some type of precleansing mechanism. Although this method is quite sensitive, it will not be examined any further unless more promising methods prove unsuitable.

(6) N, N, N', N'-Tetraphenylbenzidine [87]- Nitrogen dioxide is detected by passing a gas sample through a transparent tube containing silica gel mixed with N, N, N', N'-tetraphenylbenzidine and sulfuric acid. The reagent turns blue in contact with nitrogen dioxide, and the length of color in the tube can be used as a measure of the gas concentration.

This method utilizes N, N, N', N'-tetraphenylbenzidine which is a possible carcinogen. For this reason this method will not be examined further.

(7) Potassium Iodide, Potassium Permanganate, Starch, and Hyposulfite [88]- Nitrogen dioxide can be detected by drawing an air sample through a tube containing treated silica gel. The silica gel is prepared by impregnating 100 g of gel with 0.2 g of potassium iodide, 4.25 g of potassium permanganate, 0.05 g of starch, and 0.025 g of hyposulfite and sodium chloride.

This method is not commercially available and it utilizes highly toxic reagents. Therefore, this method will not be examined further.

(8) Potassium Iodide, Sulfanilic Acid, 1-Naphthylamine [89]- For determination of nitrogen dioxide, the sample is passed through an 8 percent solution of potassium iodide; the color is developed by diazotization of sulfanilic acid and immediate coupling with 1-naphthylamine in the presence of sodium sulfite. Color comparisons are then made with a standard set of color samples.

This method utilizes reagents that are highly toxic; also, it is not commercially available as a colorimetric detection kit. Since there are other non-commercially available methods with

low-toxicity reagents, this method will not be considered as an alternate method to the commercialy available ones.

(9) Alkaline Iodide Solution [90]- Nitrogen dioxide can be determined in air samples by absorption in alkaline iodide solution with the reduction of the nitrate and nitrite to ammonia. The ammonia is then determined titrimetrically.

This method utilizes a titration technique which would require highly trained technicians as well as extensive equipment and time. For this reason, this method does not seem to be very promising and, therefore, it will not be examined further.

(10) Matheson-Kitagawa (Nos. 117 and 117SB) [36]- Two gas detector tubes are available from this source which measure nitrogen dioxide in the concentration ranges of 1.92-1920 mg/m^3 (No. 117) and 1.92-192 mg/m^3 (No. 117SB). Each type tube requires one stroke of the sample pump and each lists chlorine, nitric oxide and ozone as interferences. The 117 detector tube has a shelf life of 1 year while the 117SB has a shelf life of 10 months when kept refrigerated at -21-10°C.

This method appears to be very promising and will be considered as an alternative to the Draeger tube (Method 12) due to its shorter (10 months) shelf life.

(11) MSA - (No. 83099) [37]- The MSA detector tube for nitrogen dioxide has a measurable range of 0.1-57.6 mg/m^3. Hydrogen sulfide and halides are listed as interferences with this tube.

This method also seems to be promising and will be reserved as an alternative to the Draeger tube (Method 12).

(12) Draeger (No. 29401) [35]- This Draeger tube is capable of detecting nitrogen dioxide as well as nitric oxide. It has a measurable concentration range of 0.96-19.20 mg/m^3 with 5 pump strokes. The standard deviation of this tube as given by the manufacturer is 15 to 10 percent. When nitric oxide is present, it is oxidized by chromium (VI) which causes a white indicating layer. With nitrogen dioxide a bluish-grey indicating layer is produced. Ozone and chlorine are listed as interferences. It has a shelf life of 2 years. This method appears to be the most promising technique available for the concurrent detection of both nitric oxide and nitrogen dioxide.

PHENYLCARBYLAMINE CHLORIDE

The physical and chemical properties of phenylcarbylamine chloride are given in Table 45. Also given in the table are the toxicological properties of phenylcarbylamine chloride. Table 46 contains a summary of information concerning each of its detection reagent systems. The toxicity and price of each reagent systems is given in Table 47. Each of the detection reagent systems are discussed in detail in the following sections.

Phenylcarbylamine Chloride Detection Reagent Recommendations

There has only been one method for the detection of phenylcarbylamine chloride found. This method involves the use of sudan red which is a carcinogen. The method might be utilized in conjunction with a colorimetric detection tube which would lessen exposure to the hazardous reagent. Effort will continue to locate a better candidate for the colorimetric detection of phenylcarbylamine chloride.

TABLE 45. PROPERTIES OF PHENYLCARBYLAMINE CHLORIDE

NAME OF SUBSTANCE:	Phenylcarbylamine chloride
MOLECULAR FORMULA:	$C_6H_5NCCl_2$
MOLECULAR WEIGHT	174.03
CAS REGISTRY NUMBER:	No information available
WISWESSER LINE NOTATION:	No information available
SYNONYMS:	A. Phenylimino phosgene B. Iso-cyanophenyl chloride
MELTING POINT:	No information available
BOILING POINT:	208.0 - 210.0°C
DENSITY/SPEC GRAVITY:	1.30 g/l at 15°C
VAPOR PRESSURE:	760 mm Hg at 208.0-210.0°C
COLOR/FORM:	A. Pale yellow B. Oily liquid
SOLUBILITY:	A. Slightly decomp. in hot water B. Decomp. in alcohol
STABILITY/SHELF LIFE:	No information available
EXPLOSIVE LIMITS:	No information available
MAJOR USES:	War gas
SPECTRAL AND OTHER PROPERTIES:	Vapor density: 6.03 g/l
TOXICITY VALUES:	A. TC_{Lo} Human inhalation 0.0498 mg/m^3/10 min. B. Lacrimator at 0.003 mg/m^3 C. Lethal at 0.05 mg/m^3/10 min. D. Acute local: ingestion 3, inhalation 3, skin absorption 3=high: may cause death or permanent injury after very short exposure to small quantities.
THRESHOLD LIMIT VALUE:	No information available
PHYSIOLOGICAL EFFECTS:	Lacrimator

(continued)

TABLE 45 (continued)

MANUFACTURING INFO:	No information available
PRODUCTION:	No information available
MANUFACTURERS:	No information available
ENVIRONMENTAL HAZARD:	Dangerous when heated to decomposition: emits highly toxic fumes of chlorides.

TABLE 46. PHENYLCARBYLAMINE CHLORIDE DETECTING REAGENTS

Reagents	Method Matrix	Interferences	Sample Type Matrix	Sensitivity	# of Operator Steps	Ref No.
1. Sudan red; Ferric chloride	chalk	Mustard gas, Phenylcarbylamine bromide	air	Not Available	2	42

TABLE 47. TOXICITY AND COST OF PHENYLCARBYLAMINE CHLORIDE DETECTING REAGENTS

Reagents	Toxicity - Acute Local[3]	Cost - $[38,39,40]
1. Sudan red; Ferric chloride	Carcinogenic; Irritant 1, Ingestion 1	25g-12.50, 2kg-8.50

0 NONE: (a) No harm under any conditions: (b) Harmful only under unusual conditions or overwhelming dosage.

1 SLIGHT: Causes readily reversible changes which disappear after end of exposure.

2 MODERATE: May involve both irreversible and reversible changes not severe enough to cause death or permanent injury.

3 HIGH: May cause death or permanent injury after very short term exposure to small quantities.

U Unknown-No valid information available on Humans

(1) Sudan Red and Ferric Chloride [42]- A mixture of one part sudan red with 1000 parts ground chalk and 3000 parts of sea sand is formulated. This mixture, when exposed to phenylcarbylamine chloride and treated with a mixture of iron (III) chloride and seven parts ground chalk, will turn from red to green. Mustard gas and phenylcarbylamine bromide are given as interferences.

PHOSGENE

The physical and chemical properties of phosgene are given in Table 48. Also included in the table are data pertaining to the toxicological properties of phosgene as well as to its manufacturers. Table 49 contains a summary of information concerning each candidate detection reagent systems. The toxicity and price of each reagent system are given in Table 50. Each of the detection reagent systems is discussed in detail in the following sections.

Phosgene Detection Reagent Recommendations

There is one commercially available colorimetric detection method, Method 15, which seems most promising for the field analysis of phosgene. This method seems to offer a high degree of sensitivity as well as selectivity. The selectivity is enhanced by a precleanse layer which screens out certain interferences. However, the magnitude of the precleanse layer screening is not given. Therefore, this will have to be determined in the laboratory.

There are two additional commercially available colorimetric methods, Methods 16 and 17, which appear promising. These methods are reserved as alternative methods in the event that Method 15 is not adequate.

There are three methods (Methods 6, 9, 11) that are not commercially available that will be considered if the three previously mentioned are insufficient for the field screening of phosgene.

TABLE 48. PROPERTIES OF PHOSGENE [3,4,25,26,27]

NAME OF SUBSTANCE:	Phosgene
MOLECULAR FORMULA:	CCl_2O
MOLECULAR WEIGHT:	98.92
CAS REGISTRY NUMBER:	75-44-5
WISWESSER LINE NOTATION:	GVG
SYNONYMS:	A. Carbonic dichloride B. CG C. Chloroformyl chloride D. Carbon oxychloride E. Carbonyl chloride F. Carbonio (ossicloruro DI) (Italian) G. Diphosgene H. Fosgeen (Dutch) I. Fosgen (Polish) J. Fosgene (Italian) K. Phosgen L. Carbon dichloride oxide M. Carbonic acid dichloride N. Carbone (oxychlorure DE) (French) O. Carbonylchloride (German) P. Koolstofoxychloride (Dutch) Q. Phosgene (DOT) R. Carbonyl dichloride
MELTING POINT:	-118°C
BOILING POINT:	8.2°C @ 760 mm Hg
DENSITY/SPEC GRAVITY:	1.432 g/l @ 0°C 4°C
VAPOR PRESSURE:	1215 mm Hg @ 20°C
COLOR/FORM:	A. Colorless, fuming liquid @ 0°C B. Colorless gas.

(continued)

TABLE 48 (continued)

	C. When liquified under pressure or refrigeration it is colorless to light yellow.
SOLUBILITY:	A. Slightly soluble in water.
	B. Freely soluble in benzene, toluene, glacial acetic acid.
	C. Freely soluble in most liquid hydrocarbons
	D. Soluble in chloroform, carbon tetrachloride
STABILITY/SHELF LIFE:	A. Slowly hydrolyzed by water.
	B. Phosgene decomp. in water & alcohol.
EXPLOSIVE LIMITS:	Mixt. of potassium & phosgene explodes when subjected to shock.
MAJOR USES:	A. War gas
	B. Intermediate, carbonylating agent
	C. Aniline dyes
	D. Chemical intermediate for toluene diisocyanate
	E. Chemical intermediate for methyl isocyanate
	F. Chemical intermediate for diphenylmethane-4.4'-diisocyanate
	G. Chemical intermediate for acyl chlorides
	H. Chemical intermediate for chloroformate esters
	I. Chemical intermediate for diethyl carbonate
	J. Chemical intermediate for dimethyl carbamoyl chloride
	K. Chemical intermediate for polymethylene polyphenylisocyanate
	L. Monomer for polycarbonate resins.
SPECTRAL & OTHER PROPERTIES:	A. Odor similar to decaying fruit @ room temp
	B. In dilute concn. has odor of green corn.
	C. Vapor density: 3.4 g/l
	D. Phosgene gas is heavier than air.
	E. Phosgene gas liquifies at 8°C.
	F. Noncombustible

(continued)

TABLE 48 (continued)

TOXICITY VALUES:	A. LC_{Lo} Rat inhalation 206 mg/m^3/30 min.
	B. LC_{Lo} Dogs inhalation 330 mg/m^3/30 min.
	C. LD_{Lo} Guinea pigs inhalation 31 mg/m^3/20 min.
	D. LC_{50} Human inhalation 3200 mg/m^3.
	E. TC_{Lo} Human inhalation 103 mg/m^3/30 mins.; toxic effects: irritant effects.
	F. Concentration greater than 250 mg/m^3 of air (62 ppm) may be fatal when breathed for one-half hr. or more.
	G. 3000 to 5000 mg/m^3 causes death within a few mins. Toxic hazard rating: acute local: irritant 3; inhalation 3. Acute systemic: inhalation 3. 3=high: may cause death or permanent injury after very short exposure to small quantities.
THRESHOLD LIMIT VALUES:	0.1 ppm (0.4 mg/m^3)
PHYSIOLOGICAL EFFECTS:	A. Pulmonary edema
	B. Hemoconcentration
	C. Bronchoconstriction
MANUFACTURING INFO:	A. Produced commercially by the catalytic chlorination of carbon monoxide & supplied in liquid form in steel cylinders.
PRODUCTION:	A. 1975-3.6×10^{11} g
	B. 62% to produce toluene diosocyanate; 24% to produce polymethylene polyphenyliso-cyanate
	C. 4% to make polycarbonate resins.
	D. 10% misc. applications (1973)
MANUFACTURERS:	A. Allied Chem. Corp., Specialty Chems. Div., Moundville, WVA
	B. EASF Wyandotte Corp., Indust Chems. Group, Geismar, LA
	C. Chemetron Corp., Group, Organic Chems. Div. La Porte, TX

(continued)

TABLE 48 (continued)

D. Dow Chem., USA., Freeport, TX

E. E.I. DuPont De Numours & Co., Inc., Elastomer Chems. Dept., Deepwater Point, NJ

F. FMC Corp., Chem. Group. Indust. Chems. Div.,Baltimore, MD

G. General Electric Co., Plastics Business Div., Engineering Plastics Product Dept., Mount Vernon, IND

H. Mobay Chem Corp., Indust Chems Div., Cedar Bayou, TX, New Martinsville, WVa

I. Olin Corp., Agricultural Chems. Div., Lake Charles, LA, Designed Products Div., Ashtabula, OH

J. PPG Indust. Inc., Chem. Div., Indust Chem Div, Barbertone, OH

K. Rubicon Chems Inc., Geismar, LA

L. Stauffer Chem. Co., Agricultural Chem. Div., Cold Creek, ALA

M. Story Chem. Corp., Ott Div., Muskegon, MI

N. Texaco Inc., Jefferson Chem. Co., Inc., Subsid., Port Neches, TX

O. Union Carbide Corp., Chems. and Plastics Div., Institute and South Charleston, WVa

P. The Upjohn Co., Polymer Chems. Div., La Porte, TX

Q. Van De Mark Chem. Co. Inc., Lockport, NY

ENVIRONMENTAL HAZARDS: No information available

TABLE 49. PHOSGENE DETECTING REAGENTS

Reagents	Method Matrix	Interferences	Sample Type of Matrix	Sensitivity	# of Operator Steps	Ref No.
1. Hexamethylenimine	titration		gas or liquid	Not Available	complex, distillation	91
2. 4,4'-Bis (dimethylamino) benzophenone	colorimetric		gas or liquid	0.5 mg/m^3	1	92
3. 4-p-Nitrobenzylpyridine; N-Benzylaniline	paper		gas	Not Available	1	93
4. p-Dimethylaminobenzaldehyde; m-Dimethylaminophenol	silica gel		gas	50 mg/m^3	1	94
5. Nitrosodimethylaminophenol	paper	specific	gas	Not Available	1	95
6 Dimethylaminobenzaldehyde; Aniline	paper		gas	41 mg/m^3	1	96
7. *Copper sulfate; Phenylhydrazine* cinnamate	paper		liquid or gas	83 mg/m^3	1	42
8. 4-(4-Nitrobenzyl) pyridine; Dimethylformamide	solution photometric		gas	Not Available	2	97
9. N-Ethyl-N-2-hydroxyethylaniline; p-Diethylbenzaldehyde; Diethyl-phthalate	paper		gas	100 mg/m^3	1	98
10. 4-(p-Nitrobenzyl)pyridine; Sodium carbonate; N-Phenylbenzylamine	crayon	HCl	gas	1 mg/m^3	1	47
11. Anabasine	paper		gas	3 mg/m^3	1	99
12. 1,2,4-Nitrosodiethylaminophenol; m-Diethylaminophenol	paper		gas	Not Available	2	83

(continued)

TABLE 49 (continued)

Reagents	Method Matrix	Interferences	Sample Type of Matrix	Sensitivity	# of Operator Steps	Ref No.
13. Diphenylamine; Dimethylamino benzaldahyde	silica gel	HCl	gas	Not Available	3	82
14. 4-(4'-Nitrobenzyl)pyridine; Mercuric cyanide; Cupric chloride; Aluminum	silica gel		gas	Not Available	2	100
15. Draeger detection tube	silica gel	Acetyl chloride Carbonyl bromide	gas	0.20 mg/m^3	1	35
16. MSA detection tube	silica gel		gas	0.40 mg/m^3	1	37
17. Matheson-Kitagawa detection tube	silica gel	Chlorine, HCl, and NO_2		0.20 mg/m^3	1	36

TABLE 50. TOXICITY AND COST OF PHOSGENE DETECTING REAGENTS

Reagents	Toxicity - Acute Local[3]	Cost - $[38,39,40]
1. Hexamethylenimine	Unknown	100g-4.30
2. 4,4'-Bis(dimethylamino)benzophenone	Unknown	25g-13.85
3. 4-p-Nitrobenzylpyridine; N-Benzylaniline	Irritant-2; Irritant-2	10g-20.45; 25g-7.75
4. p-Dimethylaminobenzaldehyde; m-Dimethylaminophenol	Unknown; Irritant-2	25g-4.40; 500g-60.00
5. Nitrosodimethylaminophenol	Probable Carcinogen	Not readily available from sources checked
6. Dimethylaminobenzaldehyde; Aniline	Unknown; Allergen 2	25g-4.40; 3kg-24.00
7. Copper sulfate; Phenylhydrazine cinnamate	Copper Compounds; Ingestion 1, Inhalation 1, Irritant 1, Allergen 1, Sulfates Irritant 3, Inhalation 3, Ingestion 3; Unknown	50g-39.00; 100g-22.50
8. 4-(4-Nitrobenzyl)pyridine; Dimethylformamide	Irritant 2; Irritant 2, Inhalation 2	10g-20.45; 500g-7.05
9. N-Ethyl-N-2-hydroxyethylaniline; p-Dimethylaminobenzaldehyde; Diethylphthalate	Unknown; Unknown; Irritant 2, Inhalation 2, Ingestion 2	500g-10.50; 25g-4.50; 100g-4.15

0 NONE: (a) No harm under any conditions: (b) Harmful only under unusual conditions or overwhelming dosage.

1 SLIGHT: Causes readily reversible changes which disappear after end of exposure.

2 MODERATE: May involve both irreversible and reversible changes not severe enough to cause death or permanent injury.

3 HIGH: May cause death or permanent injury after very short term exposure to small quantities.

U Unknown-No valid information available on Humans

(continued)

TABLE 50 (continued)

Reagents	Toxicity - Acute Local[3]	Cost - $[38,39,40]
10. 4-(p-Nitrobenzyl)pyridine; Sodium carbonate; N-Phenylbenzylamine	Irritant 2; Inhalation 2; Ingestion 3; Irritation 3;	10g-20.45; 20g-33.00; 100g-7.20
11. Anabasine	Unknown	25g-7.25
12. 1,2,4-Nitrosodiethylaminophenol; m-Diethylaminophenol	Probable Carcinogen; Unknown	Not readily available from sources checked; 100g-8.20
13. Diphenylamine; Dimethylaminobenzaldehyde	Moderate Toxcity; Unknown	100g-4.25; 25g-4.40
14. 4-(4-Nitrobenzyl)pyridine; Mercuric chloride; Aluminum	Unknown; Mercury Compounds: Irritant 3, Ingestion 3, Inhalation 2; Cyanide Compounds: Irritant 1, Copper Compounds: Irritant 1, Allergen 1, Ingestion 1, Inhalation; Chlorides-Variable; none	10g-17.00; not readily available from sources checked; 2kg-28.00; 1kg-10.50
15. Draeger detection tube	Closed tube	2.00 per tube
16. MSA detection tube	Closed tube	1.00-2.00 per tube
17. Matheson-Kitagawa detection tube	Closed tube	1.00-2.00 per tube

0 NONE: (a) No harm under any conditions: (b) Harmful only under unusual conditions or overwhelming dosage.

1 SLIGHT: Causes readily reversible changes which disappear after end of exposure.

2 MODERATE: May involve both irreversible and reversible changes not severe enough to cause death or permanent injury.

3 HIGH: May cause death or permanent injury after very short term exposure to small quantities.

U Unknown-No valid information available on Humans

(1) Hexamethylenimine [91] - The method is based on the reaction of phosgene with excess hexamethylenimine and the indirect titration of the excess after its distillation from an alkaline solution into a measured volume of 0.1 N acid. This method permits the detection of phosgene in the presence of chlorine and hydrochloric acid.

This technique utilizes a titration and a distillation procedure that would be difficult to perform in a field situation. In addition, this method would be much too time consuming for a field detection method.

(2) 4,4'-Bis (dimethylamine) Benzophenone [92] - This colorimetric detector is placed in liquid reagent system which provides reliable results in monitoring phosgene in air in the 0.41 to 41.3 mg/m^3 range.

This method appears to have the advantage that it is relatively sensitive. However, it is not commercially available. There are other non-commercially available colorimetric methods with higher degrees of sensitivity and less expensive reagents. Therefore, this method will not be examined any further.

(3) 4-p-Nitrobenzylpyridine and N-Benzylaniline [93] - This method is a rapid field test for the detection of phosgene. A 120ml air sample is drawn at a rate of 3ml/sec. through a 1cm diameter circle of Whatman No. 1 paper. The filter paper is impregnated with a solution containing 2 percent 4-p-nitrobenzylpyridine and 4 percent N-benzylaniline in benzene. The appearance of a red stain indicates the presence of phosgene. Chlorine gas, in small quantities can be removed as an interference for this test by placing a filter paper on the inlet side of the test paper. This paper is impregnated with 4 percent sodium iodide and 10 percent sodium thiosulfite.

This method will not be examined any further for several reasons. First of all, it is not commercially available. It requires a filter to remove interferences and there are other non-commercially available methods with no reported interferences. Also, its reagents are more expensive and more toxic than other methods examined.

(4) p-Dimethylaminobenzaldehyde and m-Dimethylaminophenol [94] - The indicator reagent for this method was prepared in the following manner: 20 g of activated silica gel was impregnated with 25ml of a 2 percent solution of potassium monohydrogen orthophosphate and dried 2 hours at 110°C, then 4 hours at 140°C and cooled in a desicator. The gel is then treated with a solution of 0.02 g p-dimethylaminobenzaldehyde and 0.04 g of

m-dimethylaminophenol in 20ml of cyclohexane and air dried at room temperature. The presence of chlorine and hydrochloric acid interferences can be eliminated with a packet column of silica gel impregnated with a solution of 4 percent sodium iodide and 10 percent sodium thiosulfite placed ahead of the indicator reagent. These reagents are placed in a glass tube and air is slowly drawn through the tube. This technique will detect phosgene in quantities as low as 500 mg/m^3.

This method will not be examined further for the identical reasons mentioned in Method 3. In addition, the toxicity of all the reagents is not known and the method is not as sensitive as other methods examined.

(5) Nitrosodimethylaminophenol [95] - This procedure uses filter paper that has been treated by the following method. Nitrosodimethylaminophenol (0.05 to 0.1 g) is dissolved in 50 ml of hot xylene, and M-diethylaminophenol (0.25 g) is dissolved in 50 ml of xylene. Five ml of the nitroso-compound is then mixed with 1 to 2 ml of the diethylaminophenol solution and the mixt. soaked up by filter paper. The test paper is then held in the air above the sample in question. In the presence of phosgene there will be a green coloration which is specific for this gas.

This method uses the reagent nitrosodimethylaminophenol which is a possible carcinogen. For this reason, this method will not be examined any further unless all other methods prove inadequate.

(6) Dimethylaminobenzaldehyde and Aniline [96] - This procedure is very similar to the thirteenth method discussed, but aniline is substituted for diphenylamine to make the test specific for phosgene. Filter paper is impregnated with a 95 percent alcoholic solution of p-dimethylaminobenzaldehyde and aniline. The paper will change from white to yellow in the presence of phosgene and is sensitive to 41.3 mg/m^3.

This method appears to have several advantages. These include: inexpensive reagents, reasonable degree of sensitivity, and specificity for phosgene. However, it is not commercially available as a colorimetric detection kit. It will be reserved as an alternative to the commercially available methods.

(7) Copper Sulfate and Phenylhydrazine Cinnamate [42] - For this test filter paper is impregnated with copper sulfate and dried. The paper is then dusted with phenylhydrazine cinnamate. Phosgene in a concentration as low as 82.60 mg/m^3 will produce a violet color in the presence of a drop of water.

This method does not appear to be one of the more promising methods for the field analysis of phosgene. There are other non-commercially available colorimetric methods with higher degrees of sensitivity and less expensive reagents which will be considered as alternatives to the commercially available methods.

(8) Dimethylformamide and 4-(4-Nitrobenzyl) Pyridine [97] - An air sample is passed through a dimethylformamide solution containing 4-(4-nitrobenzyl) pyridine for this approach. If phosgene is present, the quantity can be determined by comparing the solution with known concentrations at 415 nm. The optical density curve is linear up to 5 mg of phosgene per ml.

This method is not commercially available as a colorimetric detection kit. It will not be considered any further because there are other non-commercially available methods with less expensive reagents and higher degrees of sensitivity.

(9) N-Ethyl-N-2-hydroxyethylaniline, p-Dimethylaminobenzaldehyde, and Diethylphthalate [98] - A reagent solution containing 1.68 gm of N-ethyl-N-2-hydroxyethylaniline, 0.75 g of p-dimethylaminobenzaldehyde, and 2.5 ml of diethyl phthalate is prepared in 25 ml of one of the following: ethanol, acetone, or chloroform. A Whatman No. 1 filter paper is impregnated with the reagent just before use and dried. Phosgene will produce a bright blue color if present; mineral and vapors do not interfere with this method. The reagent is sensitive to 1000 mg/m^3 of phosgene.

This method seems to offer several advantages in that it is quite sensitive; its reagents are relatively inexpensive, and it is specific for phosgene. However, the reagents are moderately toxic. Also, this method is not commercially available as a colorimetric detection kit and will be considered only as an alternative to the commercially available methods.

(10) Crayon Detector [47] - The detector crayon's ingredients are: 2 percent N-4-(p-nitrobenzyl)-pyridine, 5 percent N-phenylbenzylamine, 5 percent sodium carbonate, and 88 percent neutral, amorphous, dry blanc fixe. A sufficient quantity of nitrobenzylpyridine and phenylbenzylamine in benzene solution is prepared so that the blanc fixe completely absorbs the solution and yet is completely wetted. The benzene is allowed to evaporate overnight and the mixt. is then impregnated with aqueous sodium carbonate, using enough water so that the solution is completely absorbed by the solid, and the entire mass is completely wetted. The mass is then dried and pressed into crayons. The light yellow marks made from the crayon turn red in the presence of phosgene.

The crayons remain stable at room temperature for more than a year. High concentrations of hydrogen chloride interfere with this technique.

This method has three main disadvantages as well as not being commercially available as a colorimetric detection kit. It utilizes reagents that are expensive and toxic, also hydrogen chloride interferes. Therefore, this method will not be considered any further.

(11) Anabasine [99] - This technique involves soaking filter paper in anabasine. The filter paper will then produce a purple to an intense red color on contact with an atmosphere containing as little as 3 mg/m^3 of phosgene. Other halogen compounds do not interfere with this test.

This method appears to have several advantages: it is highly sensitive, its reagents are relatively inexpensive, the end point of the detection is very distinct, and there are no interferences. However, it is not commercially available as a colorimetric detector kit. It will be reserved as an alternative to the commercially available methods.

(12) 1,2,4-Nitrosodiethylaminophenol & m-Diethylaminophenol [83] - In this method a strip of freshly moistened filter paper is exposed to a mixt. of equal parts of a 1,2,4-nitrosodiethylaminophenol and m-diethylaminophenol solutions. If phosgene is present, a distinct green color is produced.

This method utilizes 1,2,4-nitrosodiethylaminophenol which is a possible carcinogen. Therefore, it will not be examined any further.

(13) Diphenylamine, Dimethylaminobenzaldehyde [82] - In this method, one drop of diphenylamine and one drop of dimethylaminobenzaldehyde are added to a portion of silica gel. If phosgene is adsorbed, a yellow color develops. Hydrochloric acid will give the identical reaction.

This method has three disadvantages and will not be examined further. First, hydrochloric acid interferes and would have to be removed. The color change is hard to see. Also, it is not commercially available as a colorimetric detection kit.

(14) 4-4'-(Nitrobenzyl)Pyridine, Mercuric Cyanide, Cupric Chloride, Aluminum [100] - In this method, phosgene oxime is detected using silica gel granules previously used to sample the suspect gas. A methanol solution of 4-4-nitrobenzyl pyridine and mercuric cyanide is applied to the silica gel granules. The reaction is enhanced by the application of heat from cupric

chloride solution and a paper disc which contains fine aluminum particles. An exothermic chemical reaction occurs when the solution is brought into contact with the aluminum particle paper. After exposure and heating, potassium carbonate is applied causing the spot to turn an intense pink or red if phosgene is present.

This method also has three disadvantages: its reagents are highly toxic, some of the reagents are not readily available, and it is not commercially available as a colorimetric detection kit. Therefore, this method will not be examined further.

(15) Draeger (Nos. CH 19401 and CH 28301) [35]- Draeger makes two gas detection tubes for phosgene. Tube No. CH 19401 has a measurable range of 0.12 to 4.96 mg/m^3, using from 1 to 26 pump strokes. Tube No. CH 28301 has a measurable range of 1.03 to 61.95 mg/m^3 phosgene using 5 pump strokes. The relative standard deviation for both tubes is 20 to 15 percent. Carbonyl bromide and acetyl chloride are given as interferences for both tubes.

This appears to be the most promising method for two reasons: it seems to offer higher degrees of sensitivity and selectivity. If this method proves insufficient after laboratory investigation, the alternative methods will then be examined.

(16) MSA (No. 89890) [37]- This detection tube has a measurable range of 0.41 to 41.30 mg/m^3. No interferences were listed in the MSA Data Summary Sheet for their phosgene detection tube.

This method will also be considered as an alternative to the Draeger for the same reason given above, except it would have to be determined if a precleanse attachment is necessary.

(17) Matheson-Kitagawa (No. 135) [36]- The Kitagawa gas detection tube for phosgene has two concentration ranges listed. The 0.41-206.50 mg/m^3 range requires 2 pump stroke while the 0.21-41.30 mg/m^3 range requires 5 pump strokes. Chlorine, hydrochloric acid, and nitrogen dioxide are listed as interferences with this tube. Storage life for this phosgene detection tube is 8 months when kept refrigerated at -6.7 to 4.4°C. A precleanse layer would be useful to eliminate the interferences.

This method will be considered as an alternative to the Draeger tube. Because it has a shorter shelf life, it is not as sensitive and requires a precleanse attachment.

PHOSPHINE

The physical and chemical properties of phosphine are given in Table 51. Also included in this table are data pertaining to the toxicological properties of phosphine as well as to its manufacturer. Table 52 contains a summary of information concerning each of the detection reagent systems identified during the literature survey. The toxicity and price of each reagent system is given in Table 53. Each of the detection reagent systems is discussed in detail in the following sections.

Phosphine Detection Reagent Recommendations

There are three commercially available colorimetric detection methods for phosphine. The most promising technique appears to be Method 11 which utilizes the Draeger detection tube. It has a shelf life of two years, a high degree of sensitivity, is relatively inexpensive, and has a precleanse reagent to screen out several interferences. The magnitude of this screening is not mentioned so it will have to be determined in the laboratory.

The other two commercially available methods are Methods 9 and 10. These are reserved as alternatives to the Draeger tube (Method 11) in the event that it proves inadequate.

TABLE 51. PROPERTIES OF PHOSPHINE [3,4,25,26,27]

NAME OF SUBSTANCE:	Phosphine
MOLECULAR FORMULA:	PH_3
MOLECULAR WEIGHT:	34.00
CAS REGISTRY NUMBER:	7803-51-2
WISWESSER LINE NOTATION:	H3 P
SYNONYMS:	A. Hydrogen phosphide B. Phosphorus trihydride C. Celphos D. Delicia E. Detia F. Phosphine (DOT) G. Fosforowodor (Polish) H. Gas-EX-B I. Phosphoretted hydrogen J. Phostoxin
MELTING POINT:	-133°C
BOILING POINT:	-87.7°C
DENSITY/SPEC GRAVITY:	1.529 g/l @ 0°C
VAPOR PRESSURE:	20 atm @ -3°C
COLOR/FORM:	Colorless gas
SOLUBILITY:	Slightly soluble in water (0.26 vol @ 20°C)
STABILITY/SHELF LIFE:	Stable up to 55°C
EXPLOSIVE LIMITS:	A. It is a dangerous explosion hazard. B. Lowest explosion limit in air 1.79 volume % or 26 mg/m^3.
MAJOR USES:	A. Sometimes used for fumigation of grain. B. Doping agent for solid state electronic components C. Polymerization initiator

(continued)

TABLE 51 (continued)

D. Condensation catalyst

E. Chemical intermediate for phosphonium halides

SPECTRAL & OTHER PROPERTIES:

A. Vapor density: 1.17 g/l (air=1)

B. Flash point: gas

C. Density: 0.796 g/ml liquid

D. Carbide-like odor

E. Critical pressure: 65 atm; critical temp: 52°C

F. Pure phosphine is inert, but will oxidize under influence of radiation & UV light.

G. Reacts with copper, silver, gold, & their salts.

H. Combines violently with oxygen & halogens

I. Liberates hydrogen & forms phosphide when passed over heated metal

J. Forms phosphonium salts when brought in contact with halogen acids.

K. Solutions are neutral

TOXICITY VALUES:

A. LC_{50} Rats inhalation 15.6 mg/m^3/4 hr.

B. LC_{Lo} Rabbits inhalation 3550 mg/m^3/20 min.

C. LD_{Lo} Human inhalation 1420 mg/m^3.

D. 4.26 mg/m^3 safe for long term exposure, 710 mg/m^3 lethal in 30 min. 1420 mg/m^3 lethal after few breaths (for man).

E. Phosphine inhalation: survival for 4 days is ordinarily followed by recovery.

F. Phosphine is most toxic compound formed in processing of AIIIBV-Type semiconductors.

G. Toxicity rating: 6. 6= super toxic: probable oral lethal dose (human) less than 5 mg/kg; taste (less than 7 drops) for 70 kg person (150 lb).

H. Concn. of 5 ppm could be tolerated by lab animals for 2 mos. of 4-hr. daily exposures, but fatalities resulted after 7 similar exposures @ 9.94 mg/m^3.

(continued)

TABLE 51 (continued)

I. Odor threshold is 0.04 mg/m^3.

J. Value (that which can be inhaled for 8 hr. day for yr. without ill effect) accepted in Germany is 0.14 mg/m^3.

K. Tolerances & exemptions for postharvest use on crops. Phosphine from fumigation with aluminum phosphide: barley 0.14 mg/m^3; corn 0.14 mg/m^3; popcorn grain 0.14 mg/m^3; millet 0.14 mg/m^3; oats 0.14 mg/m^3; rice 0.14 mg/m^3; rye 0.14 mg/m^3; wheat 0.14 mg/m^3; sorghum 0.14 mg/m^3; grain sorghum 11.36 mg/m^3.

L. Pesticide tolerance established under Food Additives Amendment of 1958. As fumigant when derived from aluminum phosphide, in or on animal feeds & processed foods: 0.014 mg/m^3.

THRESHOLD LIMIT VALUE: 0.43 mg/m^3 air

PHYSIOLOGICAL EFFECTS:

A. Highly toxic gas analogous in its chemistry to arsine, but it does not lyse erythrocytes.

B. Phosphine is highly toxic gas especially to organs of high oxygen flow & demand. Symptoms are rapid in onset & initially characterized by respiratory, cardiac, circulatory & cerebral difficulties with extreme GI irritation followed later by renal & hepatic toxicity.

MANUFACTURING INFO:

A. Prepared by hydrolysis of metal phosphide such as calcium phosphide.

B. Formed in small quantity in putrefaction of organic matter containing phosphorus.

C. Introduced as grain fumigant in 1935 by Chemical Fabrik Delitia, Germany, by means of bag method. German Patent 667,257; 698,721 & others. Improved method (tablets) developed by Degesch in 1953 & improved again (pellets) in 1960.

D. For fumigation purposes generated by reaction of aluminum phosphide with water vapor in surrounding air. Bag method: powdered aluminum phosphide packed in moisture permeable paper envelopes. Phostoxin pellets & tablets consist of pure aluminum phosphide, ammonium carbamate, aluminum oxide & pharmaceutical paraffin.

(continued)

TABLE 51 (continued)

E. Prepared from white phosphorus & aqueous alkali hydroxide; also by treatment of PH_4I with KOH.

F. Prepared by pyrolysis of phosphorous acid.

G. Detia 6AS-EX-B-containing 57 aluminum phosphide & up to 20% aluminum stearate. Each bag develops 11 g pure hydrogen phosphide.

H. Phostoxin tablets & pellets, 1 tablet releases 1 G PH_3; 1 pellet releases 0.2 g PH_3; both disintegrate within 48-72 hrs., leaving residue of mainly aluminum oxide hydrate with 1% aluminum phosphide.

PRODUCTION: No information available

MANUFACTURERS:

A. Airco, Inc., Airco Indust. Gases Div., Santa Clara, CA, 95000.

B. G. D. Searle & Co., Will Ross, Inc., Subsid., Matheson Gas Products, Div., Cucamonga, CA, 91730, East Rutherford, NJ 07073, Gloucester, MA, 01930.

ENVIRONMENTAL HAZARDS:

A. Toxicological risk during mfr. & processing of AIIIBV-type semiconductors.

B. Phosphine is generated from calcium carbide, ferrosilicon, aluminum phosphide, sodium, zinc & other phosphides on addition of water. Raw acetylene (from calcium carbide) contains from 75 to 95 ppm of phosphine.

C. Control measures include exhaust ventilation from floor, which should be in downward direction since gas is heavier than air. Personal respirator protection also necessary; include canister-type gas masks for lower levels of contamination & otherwise, self-contained breathing apparatus safety goggles & protective clothing.

D. Threshold limit value of 0.43 mg/m^3 in air is 4 to 9 times less than minimal detectable (decaying fish) concentration of 1.42-4.26 mg/m^3 in air. Does not last long in open environment-primarily problem in closed spaces.

(continued)

TABLE 51 (continued)

E. Its offensive odor is quickly apparent in most cases. Unfortunately, odor threshold does not necessarily provide adequate warning of presence of dangerous amount.

F. Removing arsine & phosphine from waste gases of semiconductor mfr. by ozone oxidation & carbon absorption.

G. Spontaneously flammable in air if there is trace of P_2H_4 present; burns with luminous flame.

H. Auto ignition temp: 100-150°C

I. Suggested hazard identification. Flammability 4. 4= very flammable gases shut off & keep cooling water streams on exposed tanks or containers.

J. Suggested hazard identification. Health 4. 4= too dangerous to health to expose firefighters. Few whiffs of vapor could cause death, or vapor could be fatal on penetrating firefighter's normal protective clothing. Normal full protective clothing & breathing apparatus not adequate protection.

TABLE 52. PHOSPHINE DETECTING REAGENTS

	Reagents	Method Matrix	Interferences	Sample Type Matrix	Sensitivity	# of Operator Steps	Ref No.
1.	Aqueous bromide soln	Colorimetric		air	Not Available	2	101
2.	Iodine; Sodium bicarbonate	Titration		organic solvents	Not Available	2	102
3.	2-Mercaptobenzimidazole	Colorimetric		soln	Not Available	2	103
4.	Potassium permanganate; Sulfuric acid; Oxalic acid	Colorimetric	Enormous interference problem	air	Not Available	6	104
5.	Gold salt	Silica gel		air	0.14 mg/m^3	1	105
6.	Copper salts; Mercury complex	Silica gel		air	Not Available	1	106
7.	Mercuric cadmium iodide; Acetic anhydride	Paper	Hydrogen sulfide, Arsine	air	10.0 mg/m^3	2	107
8.	Silver nitrate	Paper	Arsine, Stibine	air	1.4 mg/m^3	1	108
9.	Matheson-Kitagawa detection tube	Silica gel	Arsine, Carbon monoxide, Hydrogen sulfide, and Sulfur dioxide	air	2.8 mg/m^3	2	36
10.	MSA reagent kit	Silica gel	Arsine, Stibine	air	0.036 mg/m^3	2	37
11.	Draeger detection tube	Silica gel	Arsine, Antimony hydride	air	0.142 mg/m^3	2	35

TABLE 53. TOXICITY AND COST OF PHOSPHINE DETECTING REAGENTS

Reagents	Toxicity - Acute Local[3]	Cost - $[38,39,40]
1. Aqueous bromide soln	Irritant 3, Inhalation 3, Ingestion 3	50ml-56.00
2. Iodine; Sodium bicarbonate	Irritant 3, Inhalation 3, Ingestion 3; None (unknown).	100g-10.50; 2kg-16.50
3. 2-Mercaptobenzimidazole	No information available	200g-11.50
4. Potassium permanganate; Sulfuric acid; Oxalic acid	Irritant 3, Ingestion 3, Inhalation 3; Irritant 3, Ingestion 3, Inhalation 3; Irritant 3, Ingestion 3, Inhalation 3.	2kg-19.50; 4kg-8.50; 3kg-11.50
5. Gold salt	Allergen 2	1g- 1-41.00
6. Copper salts; Mercury complexes	Irritant 1, Allergen 1, Ingestion 1, Inhalation 1, Ingestion 3, Irritant 3, Inhalation 2.	100g-1.15 - 520.00; 10g-1.50 - 157.00
7. Mercuric cadmium iodide; Acetic anhydride	No information available, however, mercury, cadmium, and iodide compounds Ingestion 3, Irritant 3, and Inhalation 2,3,3; Irritant 3, Ingestion 3, Inhalation 2	10g - 19.50 4kg - 4.50
8. Silver nitrate	Nitrates - Ingestion 2, Inhalation 2	100g-31.00
9. Matheson - Kitagawa detection tube (D)	Closed Tube	1.00-2.00 - 1 tube

0 NONE: (a) No harm under any conditions: (b) Harmful only under unusual conditions or overwhelming dosage.

1 SLIGHT: Causes readily reversible changes which disappear after end of exposure.

2 MODERATE: May involve both irreversible and reversible changes not severe enough to cause death or permanent injury.

3 HIGH: May cause death or permanent injury after very short term exposure to small quantities.

U Unknown-No valid information available on Humans

(continued)

TABLE 53 (continued)

Reagents	Toxicity - Acute Local	Cost - $[38,39,40]
10. MSA detection tube	Closed tube	1.00-2.00 - 1 tube
11. Draeger detection tube	Closed tube	1.00-2.00 - 1 tube

0 NONE: (a) No harm under any conditions: (b) Harmful only under unusual conditions or overwhelming dosage.

1 SLIGHT: Causes readily reversible changes which disappear after end of exposure.

2 MODERATE: May involve both irreversible and reversible changes not severe enough to cause death or permanent injury.

3 HIGH: May cause death or permanent injury after very short term exposure to small quantities.

U Unknown-No valid information available on Humans

(1) Aqueous Bromine Solution [101] - This method for detecting phosphine in the air is based upon the oxidation of phosphine to phosphorous pentoxide by passing the sample through absorbers containing aqueous bromine solution. After removal of bromine the phosphorus pentoxide is determined colorimetrically.

The disadvantages of this method are the high toxicity of the reagent, the high cost of the reagent, and that the method is not commercially available as a colorimetric detection kit. Therefore, it will not be examined any further as a possible field method.

(2) Iodine and Sodium Bicarbonate [102] - This method determines phosphine in organic solvents. Phosphine is oxidized with iodine in sodium bicarbonate to hypophosphorus acid. The excess iodine is then titrated with sodium thiosulfite.

This method utilizes a titration technique which would require experienced personnel and extensive equipment. For this reason this technique would not be practical for our purpose, and therefore, warrants no further examination.

(3) 2-Mercaptobenzimidazole [103] - A colorless solution of 0.5 percent 2-mercaptobenzimidazole in pyridine gives yellow-orange color changes in the presence of 0.5 ^{e}g phosphine in 1 ml of solution.

This method is not commercially available as a colorimetric detection kit, and therefore, it is not one of the more promising methods. It is also not very sensitive. For the above reasons, this method will not be considered further.

(4) Potassium Permanganate, Sulfuric Acid and Oxalic Acid [104] - Phosphine is detected in the air by collecting it in a mixture of 0.1N potassium permanganate and 5 percent sulfuric acid. The phosphate formed is decolorized with oxalic acid and an aliquot is analyzed colorimetrically.

This method has three main disadvantages. It is not commercially available as a colorimetric detection kit. Also, it utilizes reagents that are highly toxic. Last of all there is an enormous interference problem associated with this method. For these reasons, this method will not be considered further.

(5) Gold Salt [105] - Phosphine is indicated by the reduction of a gold salt impregnated on silica gel. A blue-violet color (colloidal gold) production indicates phosphine. The sensitivity of this technique is 0.14 mg/m^3 of gas.

This method is probably available in the Draeger detection tube. If so, it will be considered to be in the same category as number 11.

(6) Copper Salts and Mercury Complex [106] - By measuring the color change of copper salts containing a small amount of a mercury complex which is adsorbed on silica gel, phosphine can be detected whithin 5 minutes. There is also a possibility that this method is commercially available as a detection tube. If so, this will be considered to be in the same category as number 9.

(7) Mercuric Cadmium Iodide and Acetic Anhydride [107] - This approach uses Schleicher and Schuell No. 597 filter paper that has been impregnated with 5 percent aqueous mercuric cadmium iodide solution and allowed to dry for 30 minutes at 80°C. The paper is then protected from air and dampness by being placed in a bottle with calcium chloride. Before use the paper is moistened with 1 drop of acetic anhydride. A yellow-orange color develops in 10 minutes with from 10 to 100 mg/m^3 phosphine. Hydrogen sulfide interferes with this test by producing a similar yellow color; arsine also interferes by turning the reagent brown.

This method utilizes a highly toxic reagent which is relatively expensive. It does have a high degree of sensitivity, but is not commercially available. For these reasons, this method will not be considered further.

(8) Silver Nitrate [108] - This technique uses Whatman No. 1 filter paper that has been treated with 1 percent silver nitrate. The paper turns from brown to black with from 1.42 to 142 mg/m^3 of phosphine. Arsine and stibine interfere with this test.

This method is not commercially available as a colorimetric detection kit. Its sensitivity is also not as high as the commercially available methods. The reagent associated with this method is expensive. For these reasons, this method will not be examined further.

(9) Matheson-Kitagawa (No. 121D) [36] - The Kitagawa gas detection tube for phosphine has two measurable concentration ranges, depending on the number of pump strokes utilized. One pump stroke results in a measurable concentration range of 10-160 ppm while 5 pump strokes gives a measurable concentration range of 2.8-42 mg/m^3. Arsine, carbon monoxide, hydrogen sulfide and sulfur dioxide are listed as interferences with this tube.This tube has a 6-month shelf life.

This method is considered as an alternative to the Draeger tube. One reason is that its shelf life is about 1/4 that of the Draeger tube. It also has several interferences which would require a separate precleanse attachment. The Draeger tube is much more sensitive.

(10) MSA (Nos. 81101 and 81220) [37] - MSA does not make a gas detection tube for phosphine but they do market a reagent kit for the detection of phosphine. This kit is the identical kit MSA markets for arsine. The phosphine measurable range for this kit is 0.04-1.42 mg/m^3. Arsine is, of course, listed as an interference, as well as stibine.

This method is more costly and inconvenient, however, it will also be reserved as an alternative to the Draeger tube.

(11) Draeger (Nos. CH 31101 and CH 21201) [35] - Tube 31101 measures phosphine in the range of 0.14 to 5.68 mg/m^3 using 10 pump strokes. Arsine and antimony hydride are also indicated using this tube. The relative standard deviation of this tube is 15 to 20 percent.

Tube CH 21201 detects phosphine in the concentration range of 71 to 1420 mg/m^3 using 3 pump strokes. Arsine and antimony hydride are given as interferences. The relative standard deviation of this tube is 10 to 15 percent and shelf life for this tube is approximately two years. This is considered the most promising approach for the field detection of phosphine.

SECTION 8

SUMMARY

The objective of this study was to identify and evaluate various detection methods for the field screening of Class A poisons at uncontrolled hazardous waste disposal sites. For the purpose of the present study, the 16 Class A poisons defined by the Department of Transportation in Title 49 of the Federal Register were selected as the initial substances to be investigated. These Class A poisons are arsine, bromoacetone, cyanogen, cyanogen chloride, dichlorodiethyl sulfide (mustard gas), dichloro-(2-chlorovinyl) arsine (lewisite), diphosgene, ethyldichloroarsine, germane, hydrocyanic acid, methyldichloroarsine, nitric oxide, nitrogen dioxide, phenylcarbylamine chloride, phosgene and phosphine. The Department of Transportation defines Class A poisons as "poisonous gases or liquids of such nature that a very small amount of the gas, or vapor of the liquid, mixed with air is dangerous to life." Based on the above definition, the need for rapid field screening of Class A poisons is obvious when one considers the implication for both personal safety and transportation classification requirements.

A comprehensive literature survey was conducted on each of the poisons to identify candidate detection methods. The literature obtained on each poison was judged by the following criteria: method complexity, field adaptability, reagent shelf life, interference levels, detection sensitivity, reagent cost and reagent toxicity. Methodologies, such as portable gas chromatography, organic vapor analyzers, infrared spectrophotometry and other sophisticated instrumental techniques, were generally ruled out because of their inability to screen specifically for all Class A poisons at a given set of instrumental parameters. For example, it would be very difficult to have a one- or two-column portable gas chromatography system that would enable all 16 Class A poisons to be screened at one set of instrumental parameters. However, general detection methods such as infrared spectrophotometry could be used to determine the chemical functionality of the constituents within a complex sample. This information could be used to establish the need for additional more specific tests.

Animal testing was investigated as a means of screening for Class A poisons at hazardous waste sites. This approach would indicate the presence of potentially lethal wastes but would not be confined to the sixteen Class A poisons of interest in this study. This approach would also not be acceptable as a general screening method for toxic substances since there would be no way to establish a physiological correlation between man and the test organism on the complex variety of unknown sample types anticipated at hazardous waste sites. Test organisms can be either more or less responsive to a specific substance than man. In addition, this approach is not conducive to a rapid field screening methodology.

The use of enzyme tests as an approach to screening for Class A poisons was considered during this program. The enzyme approach involves selecting an enzyme that, when introduced to a specific compound or class of compounds, becomes inhibited in its ability to produce a specific end product. Colorimetric reactions can then be used to detect the presence of this end product. Our literature survey of this approach did not find research that had been conducted testing Class A poisons. In addition, most of the work that has been conducted has been accomplished using relatively clean aqueous matrices. It is unclear, at this point, what effect complex sample matrices may have on the inhibition of the enzymes activity. Therefore, the use of enzymes as a detection method for Class A poisons was not considered an imminently promising approach.

The Beckman Microtox™ Toxicity Monitor utilizes a specialized strain of luminescent bacteria as a bioassay organism. The total metabolic process of this bacteria is intrinsically tied to respiration but, unlike most other life forms, the end products of metabolism include an appreciable quantity of light. The metabolism of the lumenescent bacteria is influenced by low levels of toxicants which causes a corresponding change in the intensity of the organisms light output. The change of light output can be measured and used to determine the toxicological nature of the unknown sample. Obviously, the response mechanism of this method would not be tied to just Class A poisons but to all compounds which stressed the bacteria. Therefore, this approach could not be used to screen specifically for Class A poisons. The technique, however, might be useful as a means of general toxicity screening if the response factor between very toxic and slightly toxic substances could be sufficiently attenuated to reflect the differences.

The current state-of-the-art for existing general detecting methods does not provide for the specific field screening of Class A poisons. It appears that a specific detection method for each of the Class A poisons of interest to this study is the more promising approach. A convenient method for the field screening of specific volatile substances is the use of gas detection tubes. These tubes contain a granulated solid support such as silica gel with an adsorbed reagent that changes color in the presence of the species the reagent is designed to detect. A known quantity of sample gas is drawn through the detection tube and the length of the resulting discoloration is read against a pre-calibrated scale to give the concentration of the species of interest. Following is a summary of the literature survey of the more promising detection reagent systems that might be utilized with the gas detection tube concept. Gas detection tubes for several of the Class A poisons are already commercially available.

The survey showed that for hydrocyanic acid, 16 reagent detection systems lend themselves to field screening of this substance. Four of the methods considered dealt with photometric analysis, while the other procedures dealt with adsorption of hydrocyanic acid and/or the detector reagent on some type of solid support such as silica gel, filter paper, or activated charcoal. All factors considered, the commercially available Draeger detector tube for hydrocyanic acid appeared to offer the greatest potential for incorporation into field methodology. This tube has a detection range of 2.3 to 34 mg/m^3

with acidic or basic potentially interfering gases, such as hydrogen sulfide, hydrogen chloride, sulfur dioxide and ammonia, being retained in the precleanse layer.

Ten reagent systems were reported for the detection of arsine. Three of these methods involve photometric analysis; one is a titration procedure, while the other six utilize adsorption on a solid support as described above. The most promising of these methods for field screening use appears to be the Draeger arsine detector tube. This tube has a detection range of 0.16 to 195 mg/m^3. Phosphine and antimony hydride are listed as positive interferbnces. It should be noted that phosphine is also classified as a Class A poison.

A total of 16 detector reagent systems were located for the screening of ethyl and/or methyldichloroarsine. Two of these methods used a precipitate in the reagent solution as a positive result. Twelve of the methods utilized reagent-treated filter paper, while one used a coloration change made by marks of a treated crayon. The method which appears to be the most suitable for incorporation into a field test kit uses a detector tube containing silica gel which has been impregnated with a mixture of zinc sulfate and molybdic acid. This tube offers direct and sensitive detection for alkyldichloroarsines. The detection limit of the reagent is given as 2.5 µg; other closely related organo-arsenic halides and hydrogen sulfide are given as positive interferences.

For lewisite, 11 potential field screening methods were found for its detection. The most promising of these methods appears to be that which uses Michler's thioketone (4,4'-bis (dimethylamino) thiobenzophenone) as the reagent adsorbed on silica gel. This reagent system is one that is currently used by the Army in its M256 gas detector kit for the detection of lewisite.

Seven methods were identified that could be used for the field detection of cyanogen chloride. Two of these methods required photometric analysis while one involved titration. The other four approaches used reagents adsorbed on some type of solid support. The most promising approach appears to be the use of the Cyanogen chloride detector tube made by Draeger. This tube has a detection range of 0.64 to 12.8 mg/m^3. Cyanogen bromide is listed as a positive interference.

Nitric oxide and nitrogen dioxide can be detected by using the Draeger nitrous fumes detector tube. A total of 15 reagent systems were examined for the detection of nitric oxide and/or nitrogen dioxide. The Draeger tube method appears to be the most advantageous approach since both gases can be detected simultaneously and the method is commercially available.

Eleven methods appeared suitable for adaption to field screening for phosphine. One of these methods involved titration, while two utilized photometric analysis. The remaining eight methods used liquid reagents adsorbed on solid supports. The most promising method appears to be the use of the Draeger phosphine detector tube. This tube has a detection range of 0.14 to 5.68 mg/m^3. Antimony hydride and arsine, a Class A poison, are given as positive interferences.

Mustard gas was found to have 11 reagent detector systems that could be used for field screening of this compound. The most attractive of these methods appears to be silica gel impregnated with auric chloride. According to the literature, a characteristic reddish-brown coloration is obtained in the presence of mustard gas.

Only four reagent detection methods were found for the field screening of bromoacetone. The best approach for the detection of this compound appears to be a two-step method. Sodium nitroprusside is used as a detecting reagent for methyl ketones in the first step. An orange coloration of the sodium nitroprusside indicates the presence of this class of compounds. The second step is the detection of bromine using fuchsin-sulfurous acid test paper. A positive response is indicated by formation of a violet color. When both of these tests are positive, bromoacetone is assumed to be present.

Sixteen reagent systems were examined for the detection of phosgene. Three of these methods require photometric analysis while one involves titration. The remaining approaches use a reagent on solid support. The best method appears to be the used Draeger phosgene detector tube. This tube has a detection range of 0.17 to 6.2 mg/m^3, with carbonyl bromide and acetyl chloride being listed as positive interferences. Literature dealing with the detection of diphosgene stated the gas is heated 300 to 350°C in order to decompose it to phosgene, which is then detected by the above methods. The necessity of this heat treatment will have to be determined in the laboratory.

One method was located for the specific detection of cyanogen. The reagents used for this test are 8-quinolinol and potassium cyanide, which turns red in the presence of this species. In addition, cyanogen may be converted to hydrogen cyanide or cyanogen chloride and detected as these substances.

Five detection means were reported for germane. Two of these methods involved titrimetric analysis. At present, the most promising approach for field detection appears to be the use of the reagent, hydroxyphenyl fluorone, which turns an orange color in the presence of germanium.

Only one method was reported for the detection of phenylcarbylamine chloride. This method uses sudan red, ground chalk and iron (III) chloride which turns from red to green in the presence of phenylcarbylamine chloride. Sudan red is listed as a carcinogen but utilization of the reagent in a gas detection tube would lessen the possibility of exposure during use.

It is recommended that the above methods be evaluated in the laboratory as a means of screening for the Class A poison for which each system is designed. This approach should be coupled with a vapor phase or gas stripping sampling technique to determine the effect that various solvent matrices may have on each of the detection methods. General screening protocols, such as infrared spectrophotometry, should be investigated to determine if this approach is useful as means of determining when it is necessary to perform a specific test for a Class A poison.

SECTION 9

PROPOSED APPROACH FOR DETECTING CLASS A POISONS

SAMPLING OF CONTAINERS HAVING UNKNOWN WASTES

A systematic approach is necessary for sampling of unknowns for Class A poisons. Actual sampling of wastes in sealed containers for these substances may be accomplished by two practical means. Each of these methods are discussed in the following sections.

Liquid/Solid Sampling

This method would involve the actual sampling of the liquid or solids found within the container. The liquid or solid would then be systematically analyzed for each of the Class A poisons. This would be an almost impossible task in a field screening situation. It would require elaborate separatory procedures to compensate for potential interferences that might be present before colorimetric screening procedures could be applied. It could not be anticipated that samples from different containers would resemble one another as far as sample matrix is concerned. Therefore, a universal separatory procedure would have to be developed which could be applied to all matrix types. In addition, the separatory procedure would have to yield sample fractions that would be fully compatible with each detection reagent. This approach would be a major undertaking in a fully equipped laboratory even if a satisfactory universal separatory procedure could be formulated. Of necessity, the separatory procedure would have to be extremely complex requiring well-trained personnel to perform the procedure. The sampling and handling of the solid or liquid portions of unknown containers would require the use of hoods and other special safety precautions not conducive to a mobile screening operation. The purpose of this study is to develop rapid, simple screening methods that can be applied easily at remote locations.

Gaseous Sampling

The general definition for a Class A poison says that the material is of such a nature that the gas or vapor of liquid, when mixed with air, is dangerous to life. It would therefore appear that two approaches might be applied which could be used to determine if the above condition existed in containers of unknown content. The first and simplest method would be a direct analysis of the headspace from closed containers for the Class A poisons of interest to this program. The other method would entail stripping the volatile species from the unknown (with compressed air) and examining the evolved gases. Either approach would allow for greatly simplified in situ test methods to be utilized in screening for the Class A poisons. Any

interference potential should be greatly reduced. It is planned that gas sampling will be coupled with colorimetric gas detection tubes for the screening of Class A poisons in closed containers.

SEQUENTIAL SCREENING FOR CLASS A POISONS

Class A poisons can be segregated into two groups for testing purposes, arsenicals and non-arsenicals. The sequence of tests for Class A poisons is divided into two parts. Part 1 deals with arsenicals and is illustrated in Figure 1. Figure 2 shows a test matrix for non-arsenic Class A poisons discussed in Part 2. Each of the detection methods discussed below will have to be evaluated in conjunction with various types of waste matrices. For example, tests will have to be performed using various types of organic solvents to determine what effect each matrix will have on sensitivity and interference levels for each of the Class A poison detection methods. The types of matrices and nature of these tests will be determined during the initial laboratory scale-up planned for the next phase of this project.

Part 1 - Screening for Arsenical Class A Poisons.

The first test to be conducted by an operator would be for arsine. This test is conducted by analyzing a gas sample, whether headspace or stripped, with a Draeger arsine detector tube CH 25001. A positive test result is indicated by the tube changing from a white to a weak violet-grey coloration. The unknown would then be classified a Class A poison. Interferences listed for this test are phosphine (a Class A poison) and antimony hydride. If a negative result is obtained, the operator tests for either ethyl or methyldichloroarsine. These substances are screened for by using a detector tube containing zinc sulfate and molybdate. A gas sample is aspirated through the detector tube and any color change noted after a minute or so. A blue or green coloration at the intake end of the gel filling indicates the presence of ethyl or methyldichloroarsine. This test, according to literature, is specific for alkylchloroarsines. If both of these tests are negative, the operator checks for lewisite by using a Michler's thioketone detector tube. This reagent reacts with lewisite to give an intense green-blue color; ethyldichloroarsine, if not detected earlier, reacts similarly. In addition, phosgene (a Class A poison) in high concentrations will produce a purple color. Interferences for this reaction are given as chlorine and cyanogen bromide vapors; they turn the reagent a greyish color.

In the event that these three detection tests are negative the operator would assume that arsenical Class A poisons are not present and would then screen for the non-arsenical poisons.

Part 2 - Screening for Non-Arsenical Class A Poisons

Testing for non-arsenical Class A poisons is initiated by sampling the unknown gas with a variety of colorimetric detection tubes. The first test envisioned would be the use of Draeger tube No. CH 29401 for detecting nitric oxide and nitrogen dioxide. The contents of this tube will turn from white to a bluish-grey in the presence of these gases. Ozone and chlorine are

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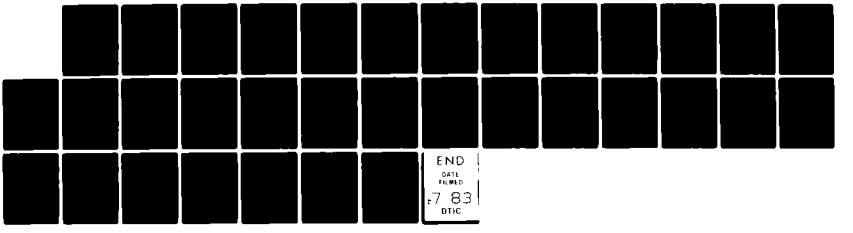

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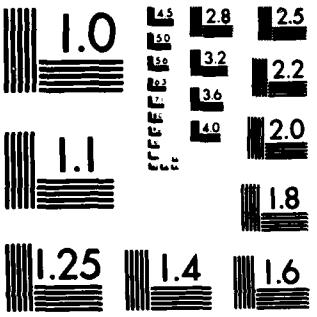

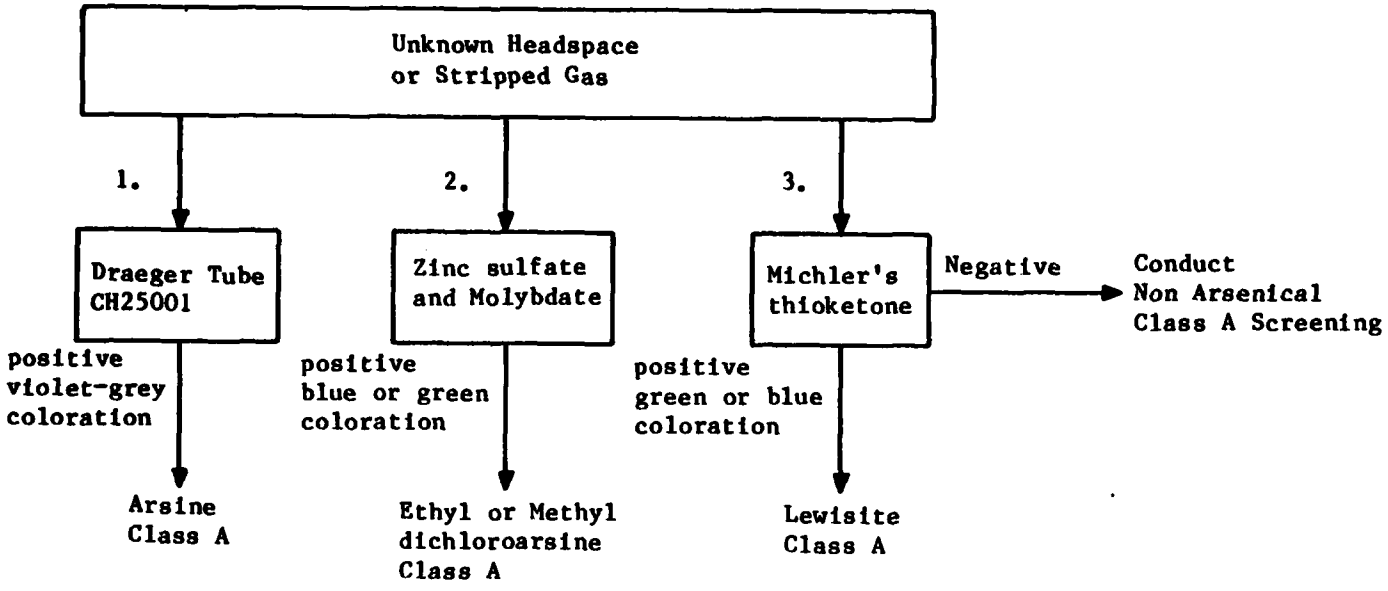

Figure 1. Preliminary arsenical test scheme.

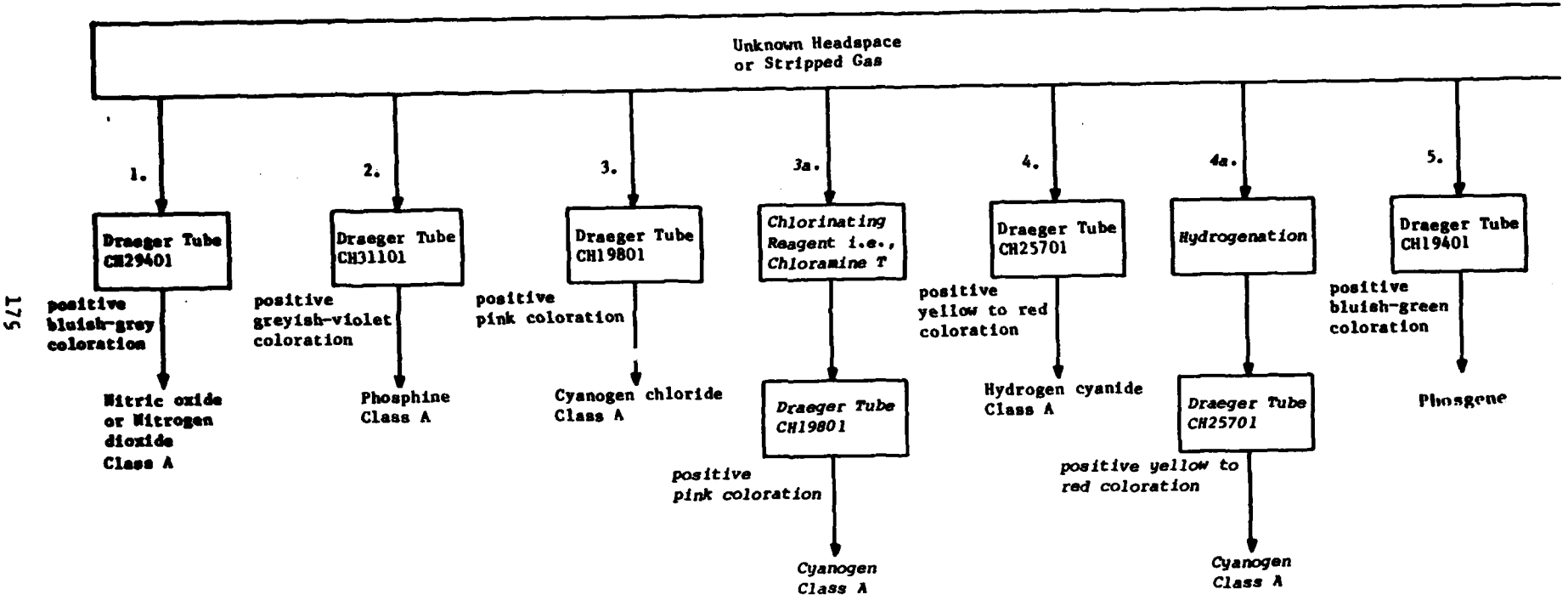

Figure 2a. Preliminary Non-arsenical test scheme

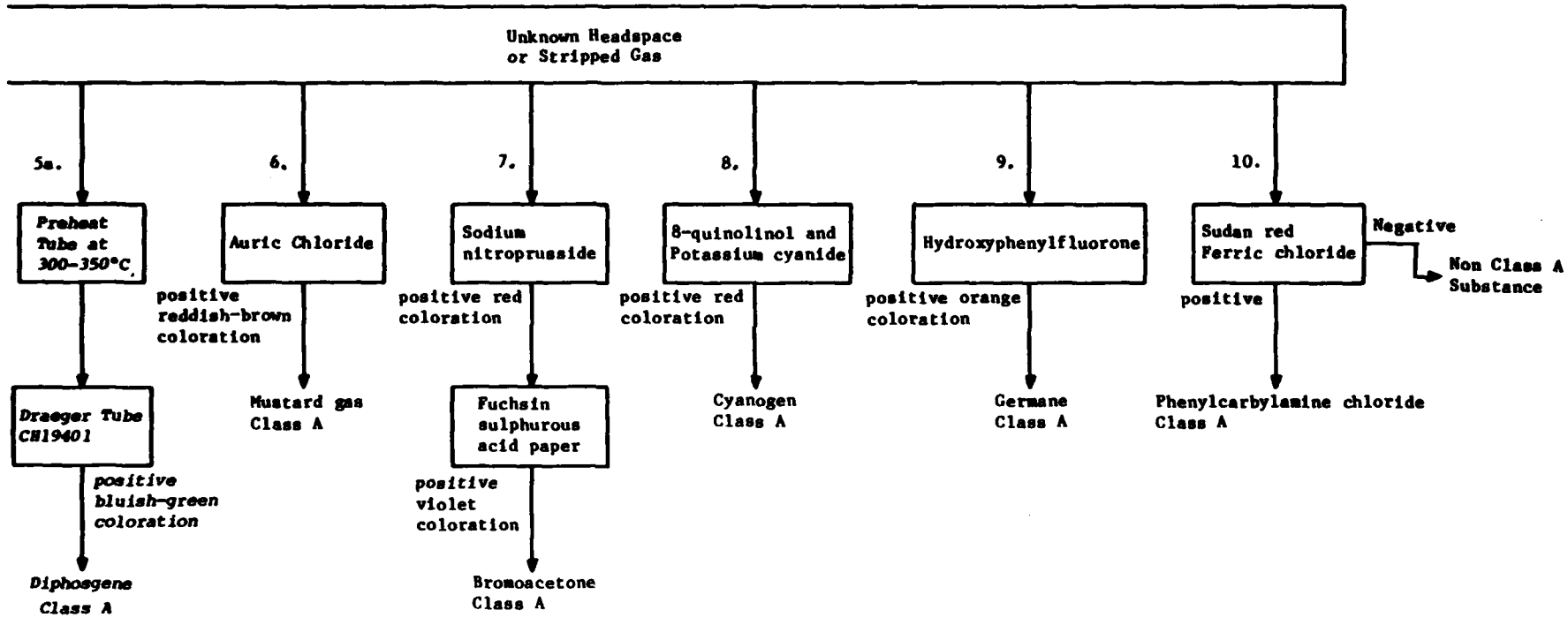

Figure 2b. Preliminary Non-arsenical test scheme

listed as the interferences for this test. After obtaining a negative result from this test the operator would screen for phosphine (test 2) using Draeger tube No. CH 31101. The white indicating layer changes to a greyish-violet coloration when phosphine is present. Arsine and antimony hydride are the listed inteferences, but with a lower sensitivity.

The operator, after obtaining negative results from the above mentioned tests, would then screen for cyanogen chloride (test 3) with Draeger tube No. CH 19801. The white indicating layer of this tube turns to a pink color when cyanogen chloride is present. Cyanogen bromide will interfere with this approach. Cyanogen detection (test 3a) may be accomplished with this tube providing a chlorinating agent, such as Chloramine T, is added to convert the cyanogen to cyanogen chloride. Actual laboratory investigation will be necessary, however, to verify this technique.

Hydrogen cyanide (test 4) would be the next gas to be screened. Draeger tube No. CH 25701 would be used to conduct this test. The indicating layer will turn from yellow to red in the presence of this gas. Cyanogen (test 4a) may also be detected using this tube by converting the cyanide groups of this compound to hydrogen cyanide. The feasibility of this method would also have to be verified in the laboratory. The final test which would be conducted using Draeger tubes would be for phosgene (test 5). Tube No. CH 19401 will detect phosgene by changing from a yellow to bluish-green coloration when brought into contact with this gas. Cyanogen bromide and acetyl chloride are the only listed interferences. Diphosgene (test 5a) may also be indicated using this tube. Literature states that, when heated at 300-500°C diphosgene will completely decomp. to phosgene. A pre-heat tube could be used in conjunction with the Draeger tube for screening diphosgene. The Draeger tube may be able to detect diphosgene without heating, but this will have to be demonstrated in the laboratory.

Mustard gas (test 6) can be detected by the use of a detector tube containing auric chloride-impregnated silica gel. According to literature, a characteristic reddish-brown coloration is obtained in the presence of this gas. The detection of bromoacetone (test 7) appears to require a two-step test approach. An alcoholic solution containing sodium nitroprusside is used to detect methyl ketones; a red coloration is produced when they are present. A positive result for this part of the test will require the operator to test for bromine using fuchsin-sulfurous acid test paper. A violet coloration of this paper indicates the presence of bromine. When both of these tests yield positive results the operator may assume that bromoacetone is present. These methods may be modified for use in detection tubes.

The unknown gas can be screened for germane (test 9) by using filter paper impregnated with hydroxyphenylfluorone. An orange coloration of the paper will indicate that this gas is present. This procedure may also prove adaptable to detector tubes. Finally phenylcarbylamine chloride (test 10) is detected by sudan red and ferric chloride diluted with chalk. If negative responses are obtained for all of the above tests the unknown wastes in question are assumed not to contain one of the Class A poisons of interest to this program.

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APPENDIX A

EXCERPTS OF TITLE 49, FEDERAL REGISTER

This section consists of excerpts from Title 49 of the Federal Register. These excerpts pertain to the shipping requirements of Class A and Class B poisons. This information was used in the comparison study discussed in Appendix B.

SECTION 173.325

CLASSES OF POISONOUS MATERIALS

(a) Poisonous materials for the purpose of this subchapter are divided into three groups according to the degree of hazard in transportation.

(1) Poison A.

(2) Poison B.

(3) Irritating material

[Amdt. 173-94. 41 FR 16081, Apr. 15, 1976]

SECTION 173.326

POISON A

(a) For the purpose of Parts 170-189 of this subchapter extremely dangerous poisons, class A, are poisonous gases or liquids of such nature that a very small amount of the gas, or vapor of the liquid, mixed with air is dangerous to life. This class includes the following:

(1) Bromoacetone.

(2) Cyanogen.

(3) Cyanogen chloride containing less than 0.9 percent water.

(4) Diphosgene.

(5) Ethyldichloroarsine

(6) Hydrocyanic acid (see Note 1 of this paragraph).

(7) [Reserved]

(8) Methyldichloroarsine.

(9) [Reserved]

(10) Nitrogen peroxide (tetroxide).

(11) [Reserved]

(12) Phosgene (diphosgene).

(13) Nitrogen tetroxide-nitric oxide mixtures containing up to 33.2 percent weight nitric oxide.

NOTE 1: Diluted solutions of hydrocyanic acid of not exceeding 5 percent strength are classed as poisonous articles, class B (see Section 173.343).

(b) Poisonous gases or liquids, class A, as defined in paragraph (a) of this section, except as provided in Section 173.331, must not be offered for transportation by rail express.

SECTION 173.327

GENERAL PACKAGING REQUIREMENTS FOR POISON A MATERIALS

(a) Cylinders must be maintained in compliance with the requirements of Section 173.34. Valves must be capable of withstanding the test pressure of the cylinders and must have taper-threaded connections directly to the cylinders (no bushings or straight-threaded connections of valves to cylinders permitted). For corrosive commodities, valves may be of the packed type provided the assembly is made gas-tight by means of a seal cap with compatible gasketed joint to the valve body or to the cylinder to prevent loss of commodity through or past the packing; otherwise the valves must be of the packless type with nonperforated diaphragms and handwheels. Each valve outlet must be sealed by a threaded cap or a threaded solid plug. The outlet caps and plugs, luting, and gaskets must be compatible with each other, the valve assembly, and the lading.

(1) The pressure of the poison gas at 130°F must not exceed the service pressure of the cylinder. Cylinders must not be liquid full at 130°F.

(2) Cylinders packed in boxes must have adequate protection for valves. Box and valve protection must be of strength sufficient to protect all parts of cylinders and valves from deformation or breakage resulting from a drop of at least 6 feet onto a concrete floor, impacting at the weakest point. A cylinder not overpacked in a box must be equipped with a protective cap or other means of valve protection which must be capable of preventing damage to or distortion of the valve if it were subjected to an impact test as follows: The cylinder, prepared as for shipment, is allowed to fall from an upright position with the side of the cap or other valve protection striking a solid steel object projecting not more than 6 inches above the floor level.

(b) Closing and cushioning. All containers must be tightly and securely closed. Inside containers must be cushioned as prescribed, or in any case when necessary to prevent breakage or leakage.

(c) No Class A poisons in cargo tanks. No "extremely dangerous poison, Class A," may be loaded into or transported in any cargo tank.

(d) It shall not be permissible to transport Class A poison if there be any interconnecting means of any character between the containers.

(e) Unless otherwise specified in this subchapter, packaging used for the transportation of any Poison A material may not be completely filled. Sufficient outage must be provided so that the packaging will not be liquid full at 130°F (55°C).

SECTION 173.328

POISON A MATERIALS NOT SPECIFICALLY PROVIDED FOR

(a) Poison A materials, as defined in Section 173.326, other than those for which special packaging requirements are prescribed in this part, must be packaged as follows:

(1) Spec. 33[1] or 3D (Section 178.41 of this chapter). Metal cylinders of not over 125 pounds water capacity (nominal). Gaskets if used between the protection cap and neck of cylinder must be renewed for each shipment even though they may appear to be in good condition. Cylinders not fitted with valve protection extension ring must be packed in wooden boxes complying as to construction, marking, and labeling, with the requirements of Section 173.25.

(2) Specification 3A1800, 3AA1800 or 3E1800 (Sections 178.36, 178.37, 178.42) cylinders.

(i) Specifications 3A and 3AA cylinders must not exceed 125 pounds water capacity (nominal). Cylinders must have valve protection or be packed in strong wooden or metal boxes as described in Section 173.327(a)(2) of this chapter.

(ii) Specification 3E1800 cylinders must be packed in strong wooden or metal boxes.

(3) Cyanogen chloride containing less than 0.9 percent water may also be packaged as prescribed by Section 173.332(a)(2) of this subchapter.

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[1] Use of existing cylinders authorized, but new construction not authorized.

SECTION 173.329

BROMOACETONE

(a) Bromoacetone, when offered for transportation by carriers by rail freight, highway, or water, must be packed in specification containers as follows:

(1) As prescribed in Section 173.328

(2) Spec. 15A, 15B, 15C, or 16A (Sections 178.168, 178.169, 178.170, or 178.185 of this subchapter). Wooden boxed with inside glass bottles or tubes in hermetically sealed metal cans in corrugated fiberboard cartons, spec. 2C (Section 178.22 of this subchapter). Bottles must contain not over 1 pound of liquid each, must be filled to not over 95 percent capacity, must be tightly and securely closed, and must be cushioned in cans with at leat 1/2 inch of absorbent material. Cans must be made of metal at least 32 gauge United States standard. Total amount of liquid in outside box must not exceed 24 pounds.

SECTION 173.332

HYDROCYANIC ACID, LIQUID (PRUSSIC ACID) AND HYDROCYANIC ACID LIQUEFIED

(a) Hydrocyanic acid, liquid (prussic acid) and hydrocyanic acid liquefied, must be packed in specification containers as follows:

(1) As prescribed in Section 173.328.

(2) Spec. 3A480, 3AA480, or 3A480X (Sections 178.36, 178.37, or 178.43 of this subchapter). Metal cylinders of not over 278 pounds water capacity (nominal); valve protection cap must be used and be at least 3/16 inch thick, gas-tight, with 3/16 inch faced seat for gasket and with United States standard form thread; the cap must be capable of preventing injury or distortion of the valve when it is subjected to an impact caused by allowing cylinder, prepared as for shipment, to fall from an upright position with side of cap striking a solid steel object projecting not more than 6 inches above floor level.

(b) Cylinders must be charged with not more than 0.6 pound of liquid for 1-pound water capacity of cylinder. Each filled cylinder must be tested for leakage before shipment and must show absolutely no leakage; this test must consist in passing over the closure of the cylinder, without the protection cap attached, a piece of Guignard's sodium picrate paper to detect any escape of hydrocyanic acid from the cylinder. Other equally efficient test methods may also be used in lieu of the picrate paper.

(c) Liquid hydrocyanic acid completely absorbed in inert material may also be shipped in specification containers as follows:

(1) Spec. 15A (Section 178.168) of this subchapter). Wooden boxes with inside containers consisting of metal cans, spec. 2N (Section 178.32 of this subchapter), not over 14 pounds water capacity each. The liquid contents of each can must not exceed 0.33 pound of liquid for 1-pound water capacity of the can. Each can containing 4 ounces or more of liquid must be fitted with fiber caps not less than 0.08 inch thick flanged about 1 inch and fitting snugly over each end of the can. Each can must be tested for leakage after being maintained at ordinary room temperature for a period of at least three weeks. Each can must have its outer surface protected against rust by the use of enamel or lacquer, or each can must be completely wrapped in waterproof paper.

(2) The box lining must consist of not more than two pieces of waterproof paper, one piece completely surrounding the contents and running

lengthwise of the box, and the other piece completely surrounding the contents and running crosswise of the box. In each instance, the wrapping must overlap at least 4 inches.

(3) Spec, 12B (Section 178.205) of this subchapter). Fiberboard boxes, constructed in accordance with requirements for a gross weight of 65 pounds but having a gross weight of not over 70 pounds, with inside containers consisting of metal cans, spec. 2N (Section 178.32 of this subchapter).The liquid contents of each can must not exceed 0.33 pound of liquid for 1-pound water capacity of the can and the total weight of liquid in each can must not exceed 41 ounces. Each can must be tested for leakage after being filled and again after being maintained at ordinary room temperature for a period of at least three weeks. Each can must have its outer surface protected against rust by the use of enamel or lacquer. Not more than twelve cans shall be packed in the outside fiberboard box and each can shall be separated from the other by 200-pound minimum test fiberboard partitions. Each box shall be provided with 200-pound minimum test fiberboard liner and top and bottom pads of the same material. In addition to the required closure of the boxes, two metal straps measuring 1/2 inch by .015 inch must be applied around the girth of each box.

SECTION 173.333

PHOSGENE OR DIPHOSGENE

(a) Phosgene or diphosgene must be packed in specification containers as follows:

(1) As prescribed in Section 173.328, the filling density (see Section 173.304(a)(2) Table Note 1) must not exceed 125 percent and a cylinder must not contain more than 150 pounds of phosgene.

SECTION 173.336

NITROGEN DIOXIDE, LIQUID; NITROGEN PEROXIDE, LIQUID; AND NITROGEN TETROXIDE; LIQUID

(a) Nitrogen dioxide, liquid, nitrogen peroxide, liquid, and nitrogen tetroxide, liquid must be packed in specification containers as follows:

(1) As prescribed in Section 173.328.

(2) Spec. 3A480 or 3AA480 (Section 178.36 or Section 178.37 of this subchapter) or 25.[1] Metal cylinders with valve removed; valve opening to be closed by means of a solid metal plug with tapered thread properly luted to prevent leakage; valve protection cap must be used and be at least 3/16 inch thick, gastight, with 3/16 inch faced seat for gasket and with United States standard form thread. Use of this container will be permitted because of the present emergency and until further order of the Department.

---

[1] Use of existing cylinders authorized, but new construction not authorized.

SECTION 173.337

NITRIC OXIDE

(a) Nitric oxide must be packed in specification containers as follows:

(1) Spec. 3A, 3AA, or 3E1800 (Section 178.36, 178.37, or 178.42 of this subchapter) cylinders designed and marked for a service pressure of 1800 pounds per square inch or higher, charged to a pressure of not more than 750 pounds per square inch at 70°F. Cylinders must be equipped with a valve of stainless steel and valve seat of material which will not be deteriorated by contact with nitric oxide or nitrogen dioxide. Containers or valves must not be equipped with safety devices of any type. Valve outlets must be sealed by a solid threaded cap or plug and an inert gasketing material.

(2) Spec. 3E1800 (Section 178.42 os this subchapter) cylinders must be packed in strong wooden boxes of such design as to protect valves from injury or accidental functioning under conditions incident to transportation. Each outside shipping container must be plainly marked "inside containers comply with prescribed specifications."

(3) Spec. 3A and 3AA (Sections 178.36 and 178.37 of this subchapter) cylinders must have their valves protected by metal caps securely attached to the cylinders and of sufficient strength to protect the valves from injury during transit, or by packing in strong wooden boxes of such design as to protect valves from injury or accidental functioning under conditions incident to transportation. Each outside shipping container must be plainly marked "inside containers comply with prescribed specifications."

SECTION 173.343

POISON B

(a) For the purposes of Parts 170-189 of this subchapter and except as otherwise provided in this Part, Class B poisons are those substances, liquid or solid (including pastes and semisolids), other than Class A poisons or Irritating materials, which are known to be so toxic to man as to afford a hazard to health during transportation; or which, in the absence of adequate data on human toxicity, are presumed to be toxic to man because they fall within any one of the following categories when tested on laboratory animals:

(1) **Oral toxicity.** Those which produce death within 48 hours in half or more than half of a group of 10 or more white laboratory rats weighing 200 to 300 grams at a single dose of 50 milligrams or less per kilogram of body weight, when administered orally.

(2) **Toxicity on inhalation.** Those which produce death within 48 hours in half or more than half of a group of 10 or more white laboratory rats weighing 200 to 300 grams, when inhaled continuously for a period of one hour or less at a concentration of 2 milligrams or less per liter of vapor, mist, or dust, provided such concentration is likely to be encountered by man when the chemical product is used in any reasonable foreseeable manner.

(3) **Toxicity by skin absorption.** Those which produce death within 48 hours in half or more than half of a group of 10 or more rabbits tested at a dosage of 200 milligrams or less per kilogram body weight, when administered by continuous contact with the bare skin for 24 hours or less.

(b) The foregoing categories shall not apply if the physical characteristics or the probable hazards to humans as shown by experience indicate that the substances will not cause serious sickness or death. Neither the display of danger or warning labels pertaining to use nor the toxicity tests set forth above shall prejudice or prohibit the exemption of any substances from the provisions of Parts 170-189 of this chapter.

SECTION 173.344

GENERAL PACKAGING REQUIREMENTS FOR POISON B LIQUIDS

(a) Closing and cushioning. All containers must be tightly and securely closed. Inside containers must be cushioned as prescribed, or in any case when necessary to prevent breakage or leakage.

(b) Packagings containing liquid material may not be completely filled. Outage must be as follows:

(1) For packagings of 110 gallons or less, sufficient outage must be provided so that the packaging will not be liquid full at 130°F, (55°C).

SECTION 173.346

POISON B LIQUIDS NOT SPECIFICALLY PROVIDED FOR

(a) Poison B liquid, as defined in Section 173.343, other than those for which special requirements are prescribed, must be packaged as follows:

(1) Spec. 5, 5A, 5B, or 5C (Sections 178.80, 178.81, 178.82, or 178.83 of this subchapter). Metal barrels or drums, with openings not exceeding 2.3 inches in diameter.

(2) Spec. 17C or 17E (Sections 178.115 or 178.116 of this subchapter). Metal drums (single-trip containers), with openings not exceeding 2.3 inches in diameter.

(3) Specification 37B (Section 178.132 or this subchapter). Metal drums (single-trip containers), welded side seams, openings not over 2.3 inches in diameter, capacity not over 10 gallons. Not authorized for transportation by air.

(4) Spec. 37A or 37B (Sections 178.131 or 178.132 of this subchapter). Metal drums (single-trip containers), with welded side seams, not over 5 gallons; authorized for Pastes only.

(5)-(6) [Reserved]

(7) Spec. 12B (Section 178.205 of this subchapter). Fiberboard boxes with glass or earthenware inside containers not over 1 quart capacity each, or with metal inside containers not over 1 gallon capacity of each. Packages containing glass or earthenware containers must not weigh over 65 pounds gross.

(8) Spec. 12D (Section 178.207 of this subchapter). Fiberboard boxes with inside container which must be glass or earthenware not over one gallon each; authorized for not more than 75 pounds gross weight; not to contain more than 4 such inside containers if their capacity is greater than 5 pints each. Use of this container will be permitted because of the present emergency and until further order of the Department.

(9) Spec. 15A, 15B, 15C, 16A, or 19A (Sections 178.168, 178.169, 178.170, 178.185, or 178.190 of this subchapter). Wooden boxes with glass or earthenware inside containers not over 1 gallon capacity each, except that inside containers up to 3 gallons are authorized when only one is packed in each outside container; or with metal inside containers, not over 10 gallons capacity each.

(11) Cylinders as prescribed for any compressed gas, except acetylene, are also authorized.

APPENDIX B

SYNOPSIS OF PACKAGING REQUIREMENTS FOR UNKNOWN SUBSTANCES

This section is comprised of a comparison study of Class A and Class B poison shipping requirements. The basis for this study is the DOT shipping requirements listed in Title 49 of the Federal Register. This study was directed towards the shipping of a totally unknown substance. In order to evaluate the material, certain assumptions were necessary. The results of this study are discussed in the following pages.

COMPARISON STUDY OF CLASS A AND CLASS B POISONS

Packaging Requirements

Hazardous material, when shipped in the United States, must meet certain requirements that are established by the Department of Transportation. These requirements differ depending upon the hazard class of the substance being shipped and are located in the Code of Federal Regulations Title 49. The following part of this report will outline some of the requirements and/or restrictions that pertain to the shipment of hazardous materials. The Department of Transportation uses the following as their order of hazard classes:

1. Forbidden
2. Radioactive material
3. Poison A
4. Flammable gas
5. Non-flammable gas
6. Flammable liquid
7. Oxidizer
8. Flammable solid
9. Corrosive material (liquid)
10. Poison B
11. Corrosive material (solid)
12. Irritating materials
13. Combustible liquid

When shipping an unknown, such as might be encountered at a hazardous waste site, it would first have to be determined that the waste is neither a forbidden nor radioactive material. A list of materials that are forbidden to be transported is given in Table B1. Beyond this the unknown waste would have to be treated and transported as a Class A poison. It should be noted that Class A poisons are forbidden to be shipped by air in the United States.

The poison A class can be broken down into two subclasses, gases and liquids. If an unknown is then to be handled as a poison A, for shipping purposes, it should first be placed in one of these subclasses.

The shipment of unknown (non-forbidden or non-radioactive) gases, illustrated in Figure B1 would require using a 3A or 3AA cylinder with a minimum service pressure of 1800 pounds per square inch. These cylinders cannot have a capacity of over 125 pounds water capacity nor exceed being filled

TABLE B-1. FORBIDDEN ARTICLES

Acetyl benzoyl peroxide

Ammonium chlorate

Charcoal screenings (wet)

Charcoal (wet)

Coal briquettes (hot)

Coke (hot)

Diethylene glycol dinitrate

Dimethylhexane dihydroperoxide (dry)

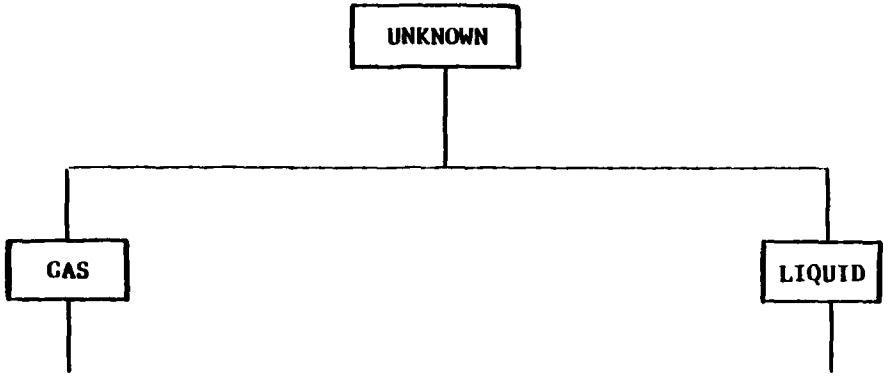
Fulminate of mercury (dry)

Hydrocyanic acid (unstabilized)

Magnesium dross (wet or hot)

Nitroglycerin (liquid, undesensitized)

Perchloric acid (exceeding 72% strength)



1. 3A or 3AA cylinders.
2. Service pressure 1800 psi (minimum)
3. 125 pounds water capacity (maximum)
4. Can be filled to not more than 0.6 pounds of liquid for each pound of water capacity and not to exceed 200 psig at 70°F.
5. Cylinder must have stainless steel valve.
6. Cylinders must be leak tested after filling.

1. Placed in glass bottles with not over one pound of liquid each and/or not filled to over 95 percent of bottle capacity.
2. Filled bottles are then placed in metal cans and cushioned by at least 1/2 inch adsorbent material.
3. Cans must be sealed air tight and placed in fiberboard cartons.
4. Cartons are then placed in wooden boxes.
5. Each wooden box must not contain over 24 pounds of liquid.

Figure B-1. Packaging of complete unknowns.

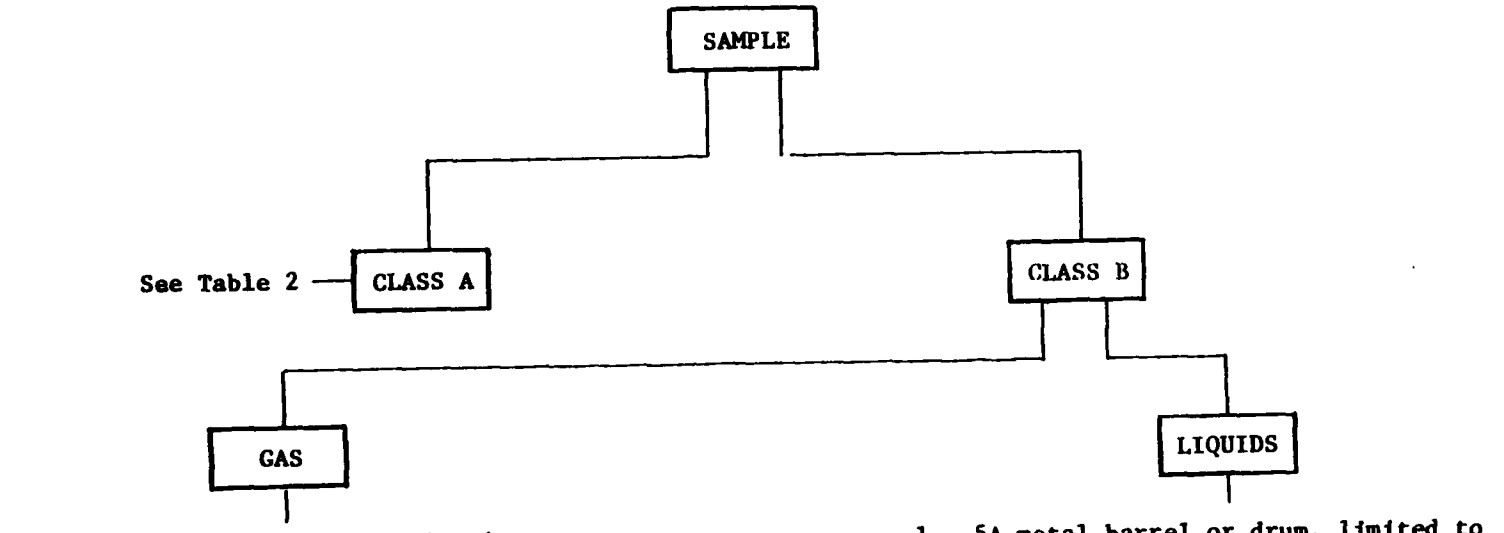
to 200 psig at 70°F and/or can only be filled with not more than 0.6 pounds of liquid for each pound of water capacity of the cylinder. In addition, each cylinder must be equipped with a stainless steel valve and leak tested. The leak test (required for the Class A poison, nitric oxide) must involve immersing the cylinder and valve in a water bath for at least 30 minutes at a temperature of 150°F. By packaging an unknown gas in this manner, all general and specific requirements for Class A gas shipments would be met.

Unknown (non-forbidden or non-radioactive) liquids shipped would also require adherence to Class A poison regulations. These regulations, also given in Figure B1, would require packaging the liquid in glass bottles which cannot contain over one pound of liquid and cannot be filled to over 95 percent of the bottle capacity. These bottles are then placed in metal cans and are cushioned by at least 1/2 inch of absorbent material. The metal cans must be sealed air tight and placed in specification 20 corrugated fiberboard cartons. These cartons are then placed in Specification 15A wooden boxes. The total amount of liquid in each wooden box must not exceed 24 pounds. By packaging an unknown liquid in this manner, all general and specific requirements for Class A liquid shipments would be met. These packaging procedures for Class A poison liquids and gases are not an absolute DOT requirement for each Class A poison but are organized using the most stringent regulations so as to cover all Class A's in general.

In the event that a waste site is screened so that Class A poisons are distinguished from Class B poisons and other hazard classes, the following shipment procedures, listed in Figure B2, could be used. Without knowing what specific Class A poison is present, those gases and liquids which are classified as Class A poisons would still have to be packaged as previously described. For non-Class A poison gases, any gas cylinder (except for acetylene) may be used for shipment. There would be no quantity limitations and the cylinder could be filled at or below the stated service pressure of the specific vessel. For shipment of non-Class A liquids, the packaging requirements would be to use a Specification 5A metal barrel or drum. The container would be limited to a 30-gallon capacity and must be constructed of not less than 12 gauge steel. The openings of these drums or barrels cannot exceed 2.3 inches in diameter and each barrel or drum must be tested, prior to filling, to a 20-pound hydrostatic test. The above packaging methods again are not absolute DOT regulations, but a combination of certain regulations in order to fulfill requirements for the hazard classes below Poison A.

Cost Factors

The advantages of screening for Class A poisons prior to shipment would be in the case of gases which were found not to be Class A poisons, any size of cylinder could be used and the shipment would not be limited to 75 pounds of the liquified gas per cylinder. In addition, stainless steel valves, which cost about $35.00 each, would not be required. Brass



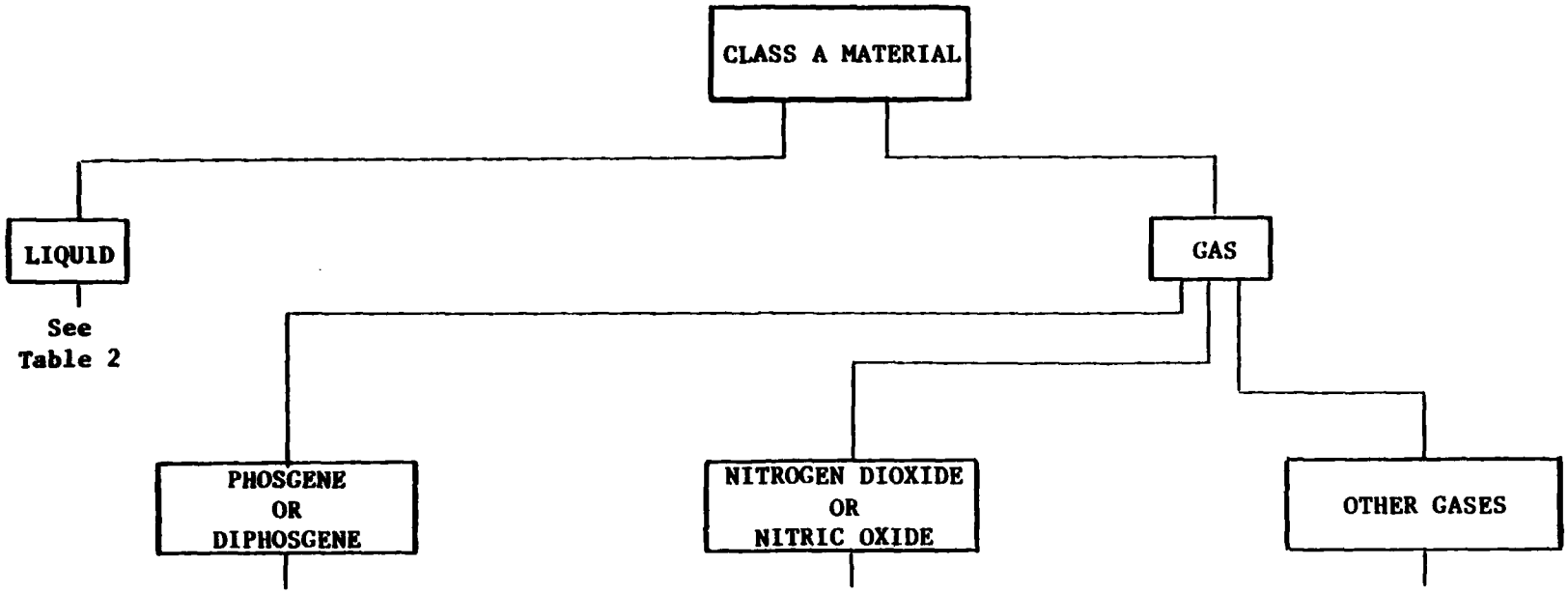
1. Any compressed gas cylinder (except acetylene) may be used.
2. Can be filled at or below cylinder's stated service pressure.

1. 5A metal barrel or drum, limited to 30 gallon capacity and constructed of not less than 12 gauge steel.
2. Drum or barrel must pass a 20-pound hydrostatic test prior to filling.
3. Openings of drum or barrels must not exceed 2.3 inches in diameter.

Figure B-2. Shipment of wastes determined to be either Class A or Class B poisons.

valves could be substituted, which cost around $7.00 to $10.00 each. Therefore, larger quantities could be shipped while the materials needed for shipment would cost less. A savings can also be realized for the shipment of liquids. Assuming the density of the unknown liquid is equivalent to water, only three gallons of the material could be placed in one wooden box as a Class A poison. The wooden box could contain 24 glass bottles which would be time consuming for the worker at a waste site to fill, not to mention safety problems associated with the exposure of the worker to an unknown. After screening for Class A poisons, a liquid found not to be a Class A poison could be shipped in 30-gallon barrels or drums. The cost of the barrel or drum would be approximately equivalent to the cost of the 24 glass bottles, fiberboard containers, and wooden box. The cost benefit would be that loading of the drum or barrel would take less time and that 10 times the quantity could be shipped per container. Assuming that it would take 15 minutes to fill a 30 gallon drum, 48 minutes to fill the individual bottles (2 minutes per bottle), and 12 minutes additional time to package the bottles one can see that packaging a Class A poison would require approximately four times the labor packaging cost of a Class B or other hazard class liquid. Actual transportation costs would be identical except that Class A poisons are forbidden for transport by air.

Workers at a hazardous waste site can go one step further, which would be to identify which specific Class A poisons are present. Shipment regulations regarding specific Class A poisons are given in Figure B3. In the case of liquids, knowing which Class A poison is present offers little more than academic interest. The procedure for packaging all Class A poison liquids is the same, so knowing what specific liquid Class A poison is present does not alter any shipment requirements. Class A gases, with the exception of phosgene, diphosgene, nitrogen dioxide and nitric oxide, can all be packaged and shipped in the same manner. This procedure would be the use of 3A or 3AA cylinders not exceeding 125 pounds water capacity with a minimum service pressure of the container. Phosgene and diphosgene also use this type of cylinder but not more than 150 pounds of either of these gases are allowed per cylinder. In addition, each cylinder must be leak tested after filling by immersing it and its valve in a water bath at 150°F for a minimum of 30 minutes. Nitric oxide and nitrogen dioxide are also shipped in 3A or 3AA cylinders but they must not be charged to over 750 psi at 70°F and these cylinders must have stainless steel valves. The cost savings that would result from knowing the specific Class A poison gas would be using brass valves then shipping any material other than nitrogen dioxide or nitric oxide. The cost benefit in not having to pressure check cylinders in the field, as is required for those containing phosgene and diphosgene, would also result in substantial savings, probably 40 to 50 dollars each. In addition, the quantity of gas per cylinder restriction would be eased for gases other than phosgene, diphosgene, nitrogen dioxide, and nitric oxide.



1. 3A or 3AA cylinder of at least 1800 psi service pressure and not exceeding 125 pounds water capacity.
2. Not to be filled to more than 150 pounds of either gas per cylinder.
3. Each cylinder must be leak tested by immersing in water, at 150°F, for a minimum of 30 minutes.

1. 3A or 3AA cylinder of at least 1800 psi service pressure and not exceeding 125 pounds water capacity.
2. Must be charged to less than 750 psi at 70°F.

1. 3A or 3AA cylinders of at least 1800 psi service pressure and not exceeding 125 pounds water capacity.
2. Filled at or below the service pressure of the cylinder.

Figure B-3. Shipment of Class A poisons.

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